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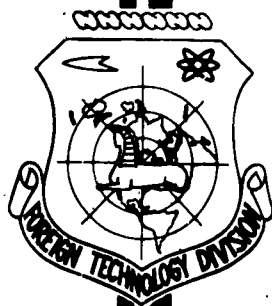
TRANSLATION

LIQUID ROCKET PROPELLANTS

By

A. Y. Seregin

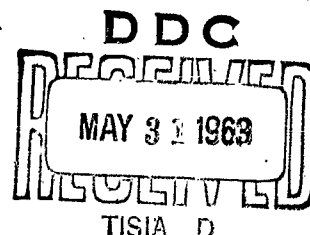
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UNEDITED ROUGH DRAFT TRANSLATION

LIQUID ROCKET PROPELLANTS

BY: A. V. Seregin

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A. V. Seregin

Liquid Rocket Propellants

Most of the rockets designed today employ chemical fuels. These are substances which as a result of chemical reactions emit heat converted by various engines, including rocket engines, into work.

The state of aggregation of these fuels may be liquid, solid, gaseous or a combination thereof. For a number of reasons rockets use only liquid or solid propellants, and, very rarely, combinations consisting of one liquid component and one solid component.

Liquid propellants are fuel mixtures, whose components, used in the rocket, are fluids.

The present book, compiled from data of the foreign literature, describes the basic properties of liquid rocket propellants and the characteristics of their application chiefly in liquid propellant engines.

The book is designed for master-sergeants, sergeants and privates of the armed forces, as well as civilians interested in the problems of rocket technology.

INTRODUCTION

In the history of humanity the twentieth century is marked by an unprecedented social progress. In our country, the largest country in the world, the building of socialist society has been completed. At the 22nd Meeting the CPSU adopted a new program -- the building of communist society.

Communism is not only the elimination of all social inequalities, but it is also the highest step in the evolution of man's spiritual and material life. The CPSU program underscores that "the achievements of Soviet science are a clear manifestation of the supremacy of the socialist order, an index of the unlimited possibilities of scientific progress and its growing role under socialism." Our country was the first in the world to employ nuclear energy for peaceful purposes; by launching artificial earth satellites it paved the way into outer space. In its program our party pledges that one of its tasks will be "the further rapid development of advance rocket technology first of all in the field of air transport and also for the conquest of outer space."

Rockets are not only means for penetrating into outer space, exploring the planets and the sun, but they are also basic weapons of our army. The CPSU program says that "the Soviet State will see to that its armed forces be powerful and be equipped with the latest means for defending the Fatherland, such as atomic and thermonuclear weapons, rockets of all ranges..."

Man had knowledge of rockets since the earliest times. There is evidence that the first rocket appeared in China many years prior to our era. Yet, despite such a long history, until the forties of this century the development of rocket-propelled vehicles was at a very low level. The lagging behind of rocket

technology during the first half of the twentieth century is chiefly due to the insufficient development of science and technology. The modern long range rockets are the result of concerted efforts by nearly all the branches of science -- physics, chemistry, radio engineering, mathematics, metallurgy, thermodynamics and others. The level reached by rocket technology in any country is an index of that country's overall development. It is for this reason that serious progress in designing rockets capable of flying hundreds and thousands of kilometers can at the present time be achieved by ^{the} only two countries ^{which are} most advanced economically and industrially, the Soviet Union and the United States of America. It is significant that in rocket technology the USSR has a long lead over the USA.

The characteristics of a rocket depend to a great extent on the proper choice of the propellant, its power and performance parameters. In a rocket ready to launch on the pad fuel represents the chief part of its weight. In long-range rockets a considerable portion of weight at ^{take-off} ^{is taken up} is taken up by the propellant. Further improvement of rocket engines is aimed in the first place at devising and applying new, more concentrated sources of energy suited for use as propellants of rocket engines.

Chapter I

GENERAL DATA

Section 1. Liquid Rocket Propellants

In liquid rocket propellants the heat to be converted to work is most frequently obtained as a result of the chemical reaction of combustion, i.e., a turbulent reaction from the oxidation of one substance by another. The oxidizing substance is called oxidizer, and the oxidized substance is called fuel.

In other heat engines using liquid propellant, including ram-jet engines, the vehicle carries only the fuel while the oxidizer (air) is taken from the surrounding medium. Vehicles driven by liquid propellant rocket engines (LPRE) carried both the fuel and the oxidizer. Hence the propellant of an LPRE is understood to be the totality (propellant composition) of substances participating in the chemical reaction releasing heat.

The substances entering into a propellant composition are called components.

Bipropellants (Fig. 1) consist of two separately stored fluids (components) of which one is the oxidizer (liquid oxygen, nitric acid, liquid fluorine, etc.) and the other the fuel (kerosene, alcohol, etc.).

Heat can be obtained, however, not only from the chemical reaction of combustion but also from such other chemical reactions as, e.g., the decomposition of certain chemical compounds, and others.

When using the decomposition reaction to release heat in the LPRE we can obtain a propellant consisting only of one component and which is called a monopropellant.

Another method for creating monopropellants is to prepare mixtures of fuel and oxidizer which under normal conditions do

not ignite spontaneously and can therefore be carried in a single container¹.

Frequently various admixtures are introduced in the propellant components, e.g., to create better conditions for the flow of the reaction, or to slow it down or stop it all together. In the former case they are called catalyzers, and in the latter inhibitors.

Depending on whether the propellant starts burning with or without an external flame, they are classified as hypergolic and anergolic propellants.

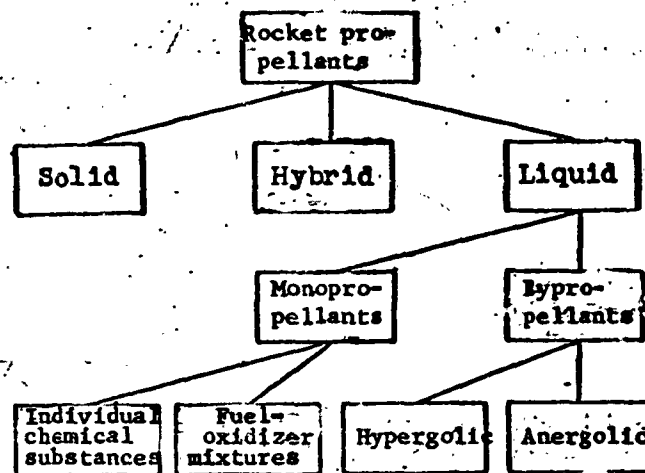


Fig. 1. Classification of liquid rocket propellants

The choice of the propellant for the LPRE depends on the purpose of the engine and of the rocket itself, and also on the state at which rocket technology finds itself at that time. To understand these questions we must acquaint ourselves with the design of the engine proper and study some general problems relating to the use of rocket propellants in LPRE's.

Section 2. Rocket Power Plant

The rocket power plant is understood to be the totality of all the units designed to set the rocket in motion. It consists of the rocket engine (RE) proper, the propellant tanks, systems for feeding the propellant into the combustion chamber and the automatic devices controlling the engine's performance.

The rocket engine consists of three basic parts (Fig. 2): injector, combustion chamber and nozzle.

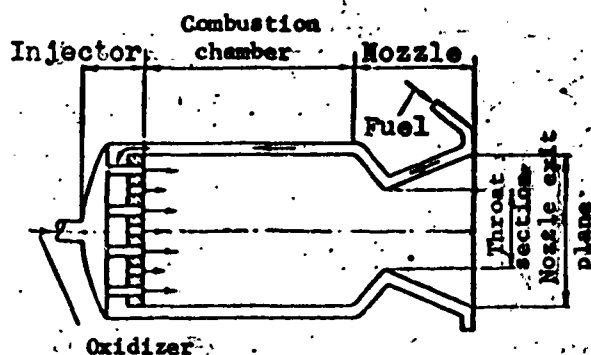


Fig. 2. Diagram of rocket engine

The engine injector contains the holes through which the propellant components are fed into the combustion chamber. They must be so placed as to ensure the required spraying and mixing of propellant components fed into the chamber. The degree of spraying and mixing of propellant components depends on the number of sprayers and on their design. The many designs exist-

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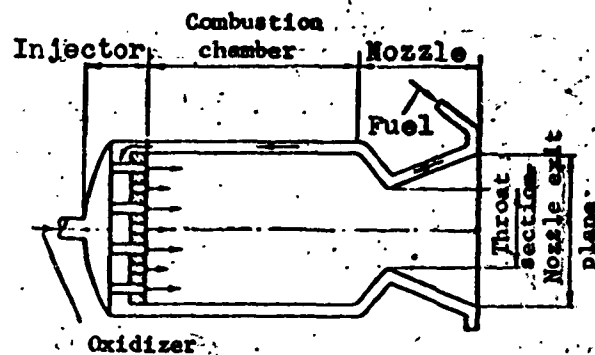


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ing can, according to the operation principle, be grouped into two classes, centrifugal and jet manifolds.

The latter are very simple in design, being small-size holes (of from 0.8 to 2.5 mm in diameter) drilled into the injector head in such a fashion that the fuel and oxidizer jets omitted by them collide, thereby providing a thorough spraying and mixing.

The advantage of jet manifolds consists in the simplicity of their design. Propellants with a high viscosity and high surface tension, however, are insufficiently atomized and intermixed when fed into the combustion chamber through jet manifolds; this leads to incomplete burning of the propellant and to a reduced performance rate of the engine.

Centrifugal manifolds are more complex in design but they ensure, with the same pressure variation as in jet manifolds, a better spraying of the propellant and, hence, a better intermixing of the components. Prior to being injected into the combustion chamber the propellant component is whirled in the centrifugal manifold, whence the fluid is ejected in the form of a thin film which readily disintegrates into droplets. Whirling of the propellant is performed either by means of a special screw inserted in the centrifugal manifold (Fig. 3, a) or by so introducing the fluid into the hollow of the manifold that prior to ejection it acquires a certain rotative speed around the manifold's axis (Fig. 3, b). This is attained by injecting the fluid laterally rather than axially. Such manifolds are known as tangential centrifugal manifolds.

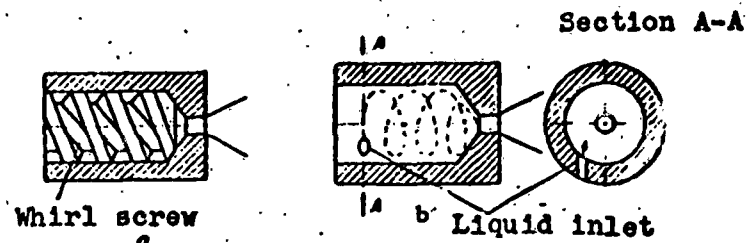


Fig. 3. Eccentric manifolds;

a - with whirl screw; b - with side inlet.

The oxidizer and fuel manifolds in the injector head are arranged in a certain order -- checkered, honey-combed, concentric (Fig. 4).

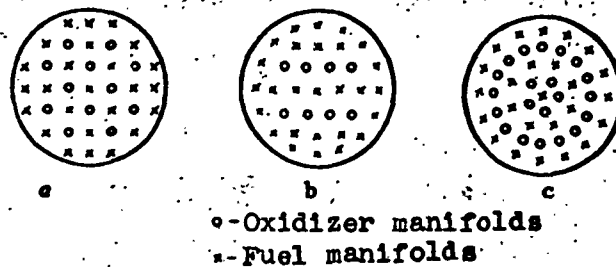


Fig. 4. Arrangement of Manifolds in Injector.

a - staggered; b - honeycomb; c) concentric

To form a protective cooling film on the combustion chamber

wall and the manifold, a number of fuel injection holes is provided on the borders (periphery) of the injector. The fuel injected from these holes mixes with the oxidizer only in part, while its bulk hits the combustion chamber wall where it forms a fluid film which in a certain distance from the ^{injector} becomes vapor. This vapor film covers the engine walls to the nozzle exit. Its purpose is to protect the combustion chamber walls and the nozzle from the action of hot gases which are the products of propellant combustion.

Most of the existing LPRE's use centrifugal manifolds since they ensure a better atomization of the fuel than jet manifolds. For propellants whose components occasionally ignite spontaneously, jet manifolds are used.

LPRE combustion chambers may be of various shapes, e.g., cylindrical, spherical, pear-shaped, etc.

The processes taking place in the combustion chamber are the atomization of propellant components, their mixing and, of course, combustion itself. Chemical energy in the propellant is converted by combustion to heat energy. Design and size of the chamber must be such that the propellant can burn up completely, i.e., that the conversion of chemical energy to heat energy be as complete as possible.

Completeness of propellant combustion depends, on the one hand, on the time the propellant stays in the combustion chamber and, on the other, on the chemical activity of propellant components, i.e., on their burning rate. The greater the propellant burning rate, the less time it is required to stay in the chamber.

Propellant residence time in the chamber can be determined by the size of reduced chamber length.

This is understood to be the ratio of combustion chamber volume $V_{ch} \text{ m}^3$ to the area of throat (narrowest) cross-section $F_{cr} \text{ m}^2$:

$$l_r = \frac{V_{ch}}{F_{cr}}$$

The greater the reduced length, the longer the propellant has to stay in the chamber, the more complete is its combustion, and the more complete will be the conversion of the propellant's chemical energy to heat energy. The reduced length of the combustion chamber, however, cannot be increased ad infinitum since for an assigned combustion pressure this will lead to an increase in the chamber's dimensions and, consequently, to increasing the engine's weight. For this reason it is sought, as a rule, to have the LPRE chamber of exactly ^{the} length required for a perfect combustion of the propellant.

Completeness of combustion in the chamber is rated by the pressure pulse. This is the ratio of the product of pressure at which propellant combustion takes place in the engine chamber times the throat cross-section area, to propellant consumption per second:

$$\beta = \frac{p F_{cr}}{G_{sec}}$$

where β is pressure pulse, in kg sec/kg;
 p is pressure in the combustion chamber, in kg/cm²;
 F_{cr} is the area throat cross-section, in cm²;
 G_{sec} is propellant flow rate per second in the engine, in kg/sec.

The greater the pressure pulse value, the more complete is propellant combustion. This value can be defined experimentally

and by computation.

Theoretical computation of pressure pulse value is done under the assumption that 100% of the propellant injected into the combustion chamber is transformed into combustion products. By comparing the theoretical pressure pulse with that determined experimentally we can define the chamber coefficient which shows the portion of propellant injected into the combustion chamber that participates in the combustion reaction:

$$\varphi_{ch} = \frac{p_{exp}}{p_{theor}}$$

Combustion chambers of modern LPRE have high values of φ_{ch} (from 0.95 to 0.98). Thus, chemical energy of the propellant in the combustion chamber is almost entirely converted into heat energy.

The nozzle at the end of the combustion chamber is a combination of a converging and a diverging cone. The purpose of the nozzle is to accelerate the gas from velocities of several tens of meters per second to velocities of a thousand meters per second, i.e., to convert heat energy released by the propellant burning in the chamber to kinetic energy of the jet (velocity energy) of gases ejected by the rocket -- the combustion products. It is in the nozzle that the reaction or thrust moving the rocket is formed.

In the converging cone of the nozzle the jet of propellant gases is accelerated to sonic velocities. In the throat the gas jet attains ^{exactly} a velocity equal to that of sound in

a gas at a temperature and with a composition in this cross-section.

The speed at which sound propagates in gases is not constant. It depends on the temperature and composition of the medium and is defined by the formula

$$a = \sqrt{kgRT},$$

where a is speed of sound, m/sec;

k is the exponential adiabatic expansion curve, depends on propellant composition;

g is acceleration of gravity, m/sec²;

R is the gas constant, kgm/degrees kg mole;

T is absolute gas temperature, °K (absolute temperature is equal to gas temperature in centigrades plus 273°, measured in degrees Kelvin).

In the diverging part of the nozzle the gas attains supersonic velocities.

As it moves through the nozzle, gas pressure constantly drops from a value equal to combustion chamber pressure, to pressure at the nozzle exit.

Pressure at nozzle exit may vary according to the geometric shape of the nozzle. Nozzle dimensions are so chosen that at the exit pressure of the expanding gas jet be equal to ambient pressure, i.e., to the pressure of the medium in which the engine performs. Under such conditions, engine performance is most economical.

As the rocket is lifted to high altitudes its engine operates in a medium with variable pressure. Variations of ambient pressure can virtually take place from 1 kg/cm² (engine performs on the ground) up to pressures equal to zero (the rocket reaches altitudes

of about 100 km and higher . Hence pressure at nozzle exit is chosen for high-altitude rockets in accordance with the altitude at which the rocket is expected to stay longest with a performing engine.

The greater the expansion to which the gases in the nozzle are subjected, the greater the conversion rate of heat energy inherent in them to kinetic energy of the gas jet.

Depending upon the composition of propellant combustion products, i.e., on the type of propellant, conversion of heat energy into kinetic energy occurs at varying degrees. Since with identical temperature and pressure the volume of various gases with a weight equal to their molecular weight is identical, it follows that the smaller their molecular weight, the larger the volume taken up by 1 kg of combustion products. Thus, the smaller the molecular weight of combustion products, the more gases are being formed (all other conditions being equal) and the more work they can perform. From this viewpoint the best propellants are those with high hydrogen content since large quantities of water vapor H_2O with a low molecular weight (18) are being formed as they burn. Propellants with a high carbon content are of the lowest quality since during combustion carbon forms carbon dioxide CO_2 with a molecular weight 44. Even lower properties will ^{be found} in propellants using metals as fuels, e.g., aluminum whose combustion is accompanied by the formation of alumina Al_2O_3 with molecular weight 102.

Gases passing from the combustion chamber into the nozzle have a specific margin of heat energy equal to the product of their specific heat and temperature. Gas temperature in the

chamber is about 3,000 to 3,500°C. At the nozzle exit it is lower than in the combustion chamber, yet it may still be sufficiently high (about 900 to 1,000°C). Thus, gases ejected from the engine through the nozzle still have a large margin of heat energy.

The distance between heat energy in the gas inside the combustion chamber and its heat energy at its exit from the nozzle into the surrounding medium corresponds to that amount of heat energy which can be converted to kinetic energy of the ejected gas jet. However, not all the heat energy difference is fully converted to kinetic energy, a part of it ^{being} lost in the nozzle to friction, heat transfer to the walls, to the formation of the jet velocity component directed perpendicularly to the engine axis and therefore not producing thrust, etc. These losses are known as nozzle coefficient. As a rule its value φ_n ranges from 0.92 to 0.95, i.e., from 8 to 5% of heat energy is lost in the nozzle for no purpose.

The product of chamber coefficients and nozzle coefficients yields the aggregate value of the engine coefficient, also called the specific impulse coefficient. The engine coefficient shows the extent to which engine design is perfect from the viewpoint of converting in it chemical propellant energy into kinetic energy of outflowing combustion products.

Section 3. Engine Cooling

As the propellant burns in the combustion chamber, exceedingly large amounts of heat are released. To compare various

engines to each other by the thermal stress in the combustion chambers, the concept of total calorific value of propellant has been established. This is understood to be the amount of heat released in a volume unit of combustion chamber where propellant combustion takes place.

Liquid propellant rocket engines are machines under heavy thermal stress. Following are total calorific values of propellants for some heat engines:

	Total calorific value, kcal/l
Modern water tube boiler	0.3 - 1.0
VRD combustion chamber	22.2 - 33.0
LPRE combustion chamber	500 - 4,700

As is seen from these data, thermal stress of rocket engines is hundreds and thousands of times higher than that of other heat engines. Hence if cooling has not been carefully devised, the material of the rocket engine will not withstand such high thermal stresses and burn out. The problem of cooling the rocket engine is complicated by the fact that only such propellant components can be used as a coolant, which, as a rule, have a lower cooling power than water, used for this purpose in nearly all the other types of heat engines.

There exist two methods of cooling rocket engines, viz., regenerative (external) and internal cooling.

Externally cooled combustion chambers and nozzles are provided with double walls. Calibrated wires or special extrusions provide between the inner and outer wall a 1 to 1.5-mm clearance

which represents the cooling jacket. One of the propellant components used as a coolant is fed to the collector in the nozzle and passes then through the cooling jacket washing the inner wall of the engine. From the space beyond the jacket the component flows to the injector and is admitted through its holes to the combustion chamber.

When flowing through the cooling jacket the propellant component is usually heated to about 100 to 110°C. Irrespective of how intensive external cooling may be, virtually no heat is lost since that removed from the engine by the coolant returns almost entirely to the combustion chamber as the heated propellant component flows into it. Hence with external cooling a minimum amount of heat should be removed from the engine to prevent pitting of the walls. But the magnitude of the heat flux removed in external cooling is limited by the properties of the propellant components. For example, in cooling with kerosene (or any other hydrocarbon fuel), at a temperature known as thermal decomposition temperature the kerosene begins to decompose.

Thermally decomposing hydrocarbon fuels separate solids with a high carbon content which precipitate on the engine walls. This deposit has a very low thermal conduction, owing to which heat transfer from the heated engine wall to the fluid sharply drops and the combustion chamber ignition plate may burn out.

Of great importance is such a property of the propellant component as boiling point with pressure in the cooling jacket. If the coolant boiling point is sufficiently low, already at low heating the fluid boils near the combustion wall surface. Surface boiling, if not too intensive, may even improve cooling.

Bubbles improve the mixing of the coolant and, hence, improve heat transfer to the fluid. But if near the cooled surface there forms a solid vapor film rather than individual bubbles, then it will prevent heat transfer from the engine wall to the coolant by acting as some sort of a thermally insulating layer because of its low heat conduction.

Rocket engines with an operation duration as short as one minute cannot always be cooled by regenerative means alone. The engines of long-range rockets operate for 1.5 to 2 min and more. To prevent the burning out of nozzle and combustion chamber walls, such engines, in addition to external cooling by one of the propellant components, must also be cooled internally.

This is effective by feeding one of the propellant components (usually the fuel) to the combustion chamber wall. Then there forms a thin fluid film which protects the wall against the immediate action of hot gases. The propellant component producing the protective film can be fed to the wall at any cross-section of the combustion chamber. The simplest way is to supply the component through holes in the border of the injector. The fuel film on the wall's surface hardly mixes with the oxidizer, hence near the injector it does virtually not participate in the combustion process. Further away from the injector the film becomes thinner on account of evaporation. At a certain distance from the injector the fluid film evaporates completely and becomes a vapor film. The latter gradually mixes with the combustion products, burns out and becomes thinner and thinner towards the nozzle exit.

In some rocket engines the protective film admitted through holes in the injector does not reach the throat because it is fully eliminated by burning-off and mixing with burning gases. Such engines are provided with several cooling belts. At a certain distance from the injector, holes are drilled into the combustion chamber walls through which the fluid component is emitted from the jacket space. These intermediate cooling belts make it possible to obtain a protective film ^{over} the entire combustion chamber length to the nozzle exit.

Unlike the case of external cooling, heat losses are involved in internal cooling. The fuel admitted directly to the combustion chamber wall does not mix with the oxidizer. As it flows along the wall to the nozzle exit, the fuel burns out only in part, while most of it ^{is expelled} by the nozzle in the form of vapor. Consequently the combustion chamber coefficient which indicates the part of the propellant injected into the engine which burns out completely, decreases, i.e., fuel recovery rate decreases. Rocket engines are therefore chiefly externally cooled, and internal cooling is used only as secondary to regenerative cooling.

Section 4. Analysis of Rocket Propellant Efficiency

Propellants are a source of energy which through the engine is imparted to the vehicle. Velocity and range of the vehicle with a specific propellant load depend on the efficiency of the propellant. There are two methods for evaluating this efficiency, the thermodynamic and the ballistic method. The thermodynamic analysis disregards the vehicle's structural characteristics.

The method consists in determining the thrust of the engine per one kilogram of propellant consumed in one second. This quantity is known as specific impulse. The propellant's efficiency is directly proportional to its specific impulse.

The latter can be determined by either test, directly in the engine, or theoretically by computation. The value of specific impulse depends not only on the propellant's power parameters but also on the combustion products expansion rate ^{as} they are ejected from the nozzle. Thus a propellant tested in ^{an} engine having identical pressure at nozzle exit (e.g., ambient pressure 1 atmosphere) and a different pressure in the combustion chamber, develop a specific impulse all the greater the higher ^{the} pressure is in the combustion chamber. Hence the power parameters of various propellants must be compared to one another ^{under} identical application conditions in the engine.

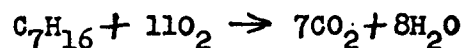
The power parameters of bi-propellants also depend on the ratio at which the components are admitted into the engine's combustion chamber. That component ratio at which the oxidizer just suffices for a complete combustion of the fuel (carbon up to CO_2 and hydrogen up to H_2O) is said to be stoichiometric. It is known, however, that to obtain maximum specific impulse the propellant components should be injected into the engine not at a stoichiometric ratio but with a certain fuel surplus.

Evaluation by test of the efficiency of rocket propellants is carried out on stands by measuring the thrust developed by the engine and propellant component flow rate per second. Engine thrust is defined for various ratios of oxidizer and fuel, and thus is found the optimum ratio which with a given propellant

consumption yields maximum thrust. Specific impulse is defined as the ratio of thrust developed by the engine to propellant flow rate per second, i.e., the aggregate oxidizer and fuel flow rate per second.

Specific propellant impulse is but slightly dependent on the engine's design features. For this reason specific impulse calculated theoretically is in good agreement with that experimentally determined at the stand.

To determine the propellant's performance parameters, by computation we must know the composition and temperature of combustion products formed in the engine's combustion chamber at a prescribed pressure. If we know the composition of the oxidizer and the fuel, i.e., the number of atoms constituting their molecules, we can write the equation of the combustion reaction taking place in the combustion chamber and thus determine the composition of combustion products. For example, if kerosene is burned in liquid oxygen at a stoichiometric ratio of components, the combustion reaction equation takes the form:



kero-	oxy-	carbon	water
sene	gen	dioxide	vapor

From this equation we can easily determine the amount of combustion products formed, that is, the amount of carbon dioxide and water vapor.

Since the amount of heat released by the formation of carbon dioxide and water vapor is known, the overall heat generated by combustion reaction also becomes known.

Such a simplified computation, however, gives only an approximate answer to the question as to the composition of combustion

products of the rocket propellant and its efficiency. When the propellant burns in the engine's combustion chamber, temperatures of about 3,000 to 3,500°C are generated. At such temperatures the fuel oxidization products (carbon dioxide and water vapor) dissociate. This process is known as thermal dissociation. The higher the propellant ^{combustion} temperature, the greater the rate of gas dissociation. The latter forms a number of new gaseous substances such as carbon monoxide CO, nitric oxide NO, the radical OH, atomic and molecular hydrogen H and H₂, atomic and molecular nitrogen N and N₂ and others. As pressure in the combustion chamber increases at the same temperature, dissociation of combustion products decreases.

Thus propellant combustion in rocket engine combustion chambers is associated with the formation of combustion products which are a mixture of various gases. Dissociation, i.e., decomposition of complex molecules into simpler and lighter ones, on the one hand lowers the temperature in the chamber since heat is being absorbed, and on the other hand it forms gases with a molecular weight smaller than that of the initial combustion products. To compute the temperature and composition of gases (propellant combustion products) is quite laborious. After this has been completed, specific impulse which is the basic parameter of the efficiency of rocket propellants, is defined by the formula

$$P_{sp} = \sqrt{\frac{2RT}{g} \frac{k}{k-1} \left[1 - \left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} \right]}, \quad (1)$$

where R is the gas constant, kg-cm/degrees, kg mole;

T is combustion product temperature in the chamber, °K;

k is adiabatic pressure index;

p_e is pressure at exit plane of nozzle, kg/cm^2 ;

p_c is combustion chamber pressure, kg/cm^2 .

The

A specific impulse calculated in the above fashion is ideal.

It could be obtained if there were no losses in the combustion chamber or the nozzle. But since there are always losses in the combustion chamber and the nozzle, and their values are usually known for engines of specific designs, actual specific impulse is found ^{to be} the product of theoretical specific impulse

$P_{sp,th}$ times coefficient φ which considers the losses in the nozzle and the combustion chamber;

$$P_{sp} = P_{sp,th} \varphi$$

where $\varphi = \varphi_n \varphi_c$.

We see from formula (1) that specific impulse depends, on the one hand, on the expansion rate of gases in the nozzle as they are expelled from the engine, which is considered by the factor

$$\sqrt{1 - \left(\frac{p_a}{p_c}\right)^{\frac{k-1}{k}}}, \quad \text{and, on the other hand, on the type of propellant.}$$

With one and the same expansion rate of combustion products in the nozzle, specific impulse depends only on the characteristics of the propellant employed. As is seen from the formula, specific impulse is the greater, the higher ^{the} propellant combustion temperature; this temperature, however, is proportional to propellant calorific power. Hence the chief specification for a rocket propellant is high calorific power.

Specific impulse is also proportional to the square root of R (the gas constant of combustion products) which is $R = 848/\mu$, i.e., it is equal to the ratio of the universal gas constant to

the molecular weight of the given gas. This means that with calorific values specific impulse will be higher in those propellants whose combustion products have a smaller molecular weight.

Thus, the propellant requirements specified earlier are now also theoretically corroborated.

Ballistic propellant evaluation. The chief propellant efficiency characteristic for the ballistic evaluation is the range of the rocket or its maximum velocity at the end of the active sector, i.e., at the instant of total propellant utilization. Maximum rocket velocity can be defined from the Tsiolkovski equation

$$V = 2.3 \frac{P_{sp}}{g} \lg \left(1 + \frac{G_p}{G_{w.o.}} \right) \quad (2)$$

where V is rocket velocity at the end of active sector, m/sec;

\lg is logarithm sign;

g is acceleration of gravity, m/sec²;

P_{sp} is specific impulse of engine operating with a given propellant, kg sec/kg;

G_p is weight of propellant carried by the rocket at take-off, tons;

$G_{w.o.}$ is rocket weight without propellant, tons.

The weight of propellant in the rocket can be represented as the product of mean specific propellant weight d_p and the volume of rocket tanks Q :

$$G_p = Q d_p$$

Then the Tsiolkovski equation can be written

$$V = 2.3 \frac{P_{sp}}{g} \lg \left(1 + \frac{Q d_p}{G_{w.o.}} \right)$$

The ratio of tank volume to dry weight of rocket is the rocket

design characteristic (design index or weight quality indicator of the rocket). In comparing rocket propellants with one and the same weight quality indicator the latter can be set equal to unity in the velocity equation. In so doing the Tsiolkovski equation (2) permits to determine the effect of the propellant parameters alone on maximum rocket velocity at the end of the active sector:

$$V = 2,3 \frac{P}{\rho} \lg(1 + d_p).$$

i.e., the velocity of ... the same rocket propelled by different fuels depends on two indicators, specific impulse of propellant and density of components. A propellant is all the more effective, the greater its specific impulse and its density.

Computations show that for long-range rockets it is more expedient to choose propellants with high performance parameters, i.e., propellants with high specific impulses, even if their density is low; with increasing rocket range, propellant density gains in importance.

Section 5. Propellant Supply Systems

Rocket propellant tanks are designed to hold the propellant required for engine supply. From the tanks the propellant is fed through conduits into the combustion chamber.

To inject the propellant into the combustion chamber, it must be imparted a pressure in any case slightly higher than combustion chamber gas pressure. Propellant pressure should, moreover, be increased by a quantity required for its atomization and mixing, and also by the amount of frictional losses and propellant whirls in the lines. The propellant can be fed into the engine either by forcing it out of the tanks (pressure feed system) or by

pumping it from the propellant tanks and creating the required feed pressure in the lines behind the pumps (pump feed system).

In the former feed system the required pressure in the propellant tanks can be achieved in various fashions. There is, for example, the pressure feed system with liquid propellant pressure accumulator (LPA) or with a gas producing grain bottle (GPB).

Gas pressure feed system (Fig. 5). From the tanks the propellant is displaced with a gas (usually air) and transferred into the engine combustion chamber. If air is used, the feed system is called one with an air pressure accumulator (APA). The vehicle carries the gas in a tank at high pressure (about 200 kg/cm^2).

From the high pressure tank the gas is fed to the propellant tanks through a regulator which reduces gas pressure in the tank to values required in the propellant tank and, moreover, maintains the propellant component tanks at a constant level.

The drawback common to all gas pressure feed systems is the gas load of propellant tanks where during engine performance a pressure of 10 to 15 kg/cm^2 (which exceeds that in the combustion chamber) must be maintained. This requires tanks with strong, thick walls. Propellant tanks in rockets with gas pressure feed systems are therefore very heavy and take up a considerable portion of the vehicle's total weight. As combustion chamber pressure increases, the weight of propellant tanks increases as well.

Gas pressure propellant feed systems are only used with rocket power plants performing at combustion chamber pressures not exceeding $20 \text{ to } 25 \text{ kg/cm}^2$.

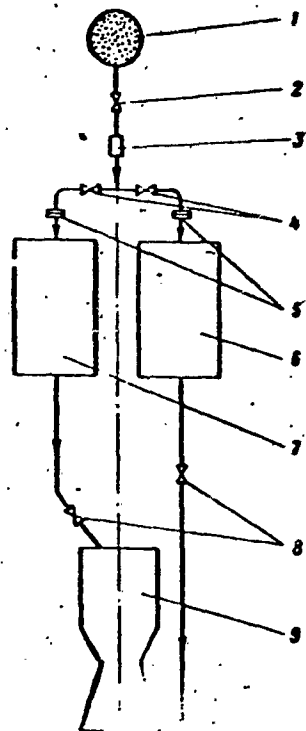


Fig. 5. Schematic of gas pressure feed system

1 - High pressure gas tank; 2 - Start valve; 3 - Pressure regulator; 4 - Check valve; 5 - Unobstructed blowback diaphragm; 6 - fuel tank; 7 - Oxidizer tank; 8 - Cutoff valves; 9 - Engine

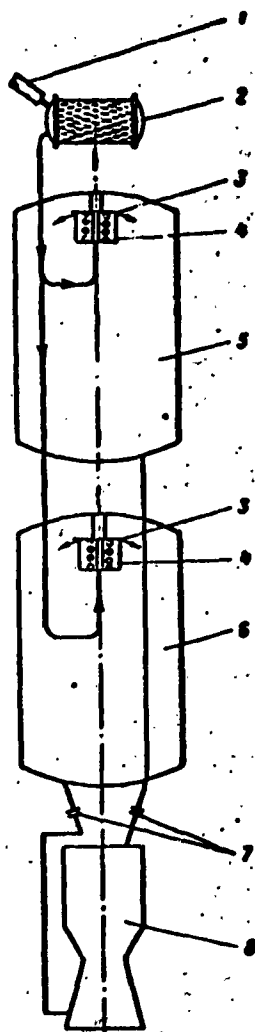


Fig. 6. Schematic of heat system with gas producing grain bottle.

1 - Start valve with electric igniter; 2 - Gas producing grain bottle; 3 - Gas reflector; 4 - Check valve; 5 - Oxidizer tank; 6 - Fuel tank; 7 - Pressure blowback diaphragms; 8 - Engine

Feed systems with gas producing grain bottles (Fig. 6).

The propellant components are forced into the engine by a gas formed by the burning of a powder charge (shashka). Its volume is considerably smaller than that of the gas generated by its burning, even if that gas is compressed to a pressure of 200 kg/cm^2 . Thus, gas producing grain bottles take up considerably less room than high pressure gas tanks if the amount of gas in the tank is equal to that generated by the powder charge (shashka) of the gas producing grain bottle. The latter also weighs considerably less than a tank filled with gas at a pressure of 200 kg/cm^2 .

The gas producing grain bottle is attached directly to the top part of the propellant tank. The grain is ignited by a pyrotechnic explosion produced, in turn, by an electric spark.

Burning of the powder (shashka) is so regulated as to maintain a constant pressure in the propellant tank during engine performance.

The gas formed by the burning powder is qualitatively quite different from that which forces out the propellant components in the gas pressure feed system. Powder burns at a temperature of about $2,200^\circ\text{C}$. The powder gases are fed into the propellant tank at a temperature of 800 to 900°C . It is known that gas increases its volume per unit weight as its temperature increases. Hence extrusion of the same amount of propellant components by means of a gas producing grain bottle will require less gas than if this is done by means of a gas pressure feed system. Gas flow will decrease approximately by the same ratio as that by which powder gas temperature exceeds that of the gas in the pressure tank.

Powder gases are the products of powder combustion. Since

powder contains less oxidizer than required for complete fuel combustion, incomplete combustion products will always be present in powder gases. Powder gases may finish burning when they come in contact with liquid oxidizers or yield explosive mixtures if they mix at a certain ratio with oxidizer vapors. The use of gas producing grain bottles to feed oxidizer or monopropellant into the engine is not always safe.

Since powder combustion is accompanied by the formation of a reducing gas, i.e., a gas in which the fuel is not completely oxidized, the use of gas producing grain bottles for the feeding of fuel into the engine is less dangerous. There is virtually no chemical interaction between the fuel and the reducing gas. It should be borne in mind, however, that powder gases enter propellant tanks at high temperatures. Contact of these hot gases with certain propellant components during pressurization may bring about the decomposition of the fuel with concomitant heat release and the formation of gaseous products. For example, a fuel like hydrazine N_2H_4 if heated to 480° decomposes into ammonia, hydrogen and nitrogen.

As with any pressure feed system, also here the tank walls are subjected to heavy gas pressure loads. Moreover, they are additionally heated by hot powder gases. The strength of metals sharply decreases with heating, hence when using gas producing grain bottles the propellant tank walls must be thicker than with gas pressure feed systems, all other conditions being equal, and the tanks themselves must be heavier. Gas producing grain bottles are used only with engines performing at low combustion chamber pressures.

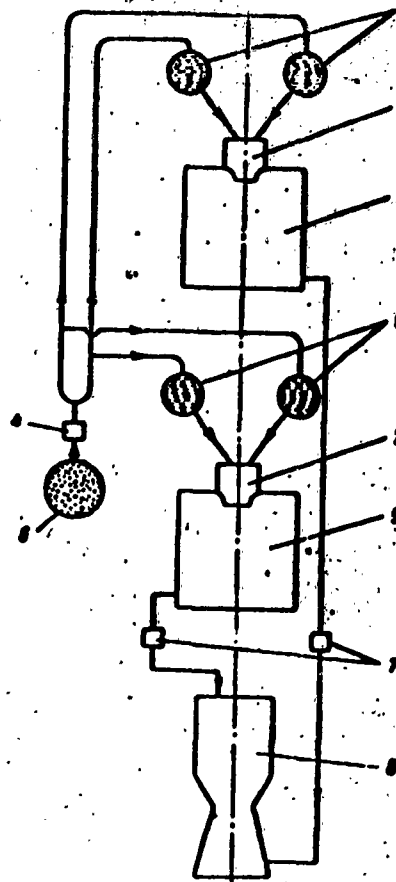


Fig. 7. Feed system with liquid-propellant pressure accumulator

1 - Auxiliary propellant tanks; 2 - Gas generator; 3 - Main fuel tank; 4 - Pressure regulator; 5 - Main oxidizer tank; 6 - Compressed air tank; 7 - Cutoff valves; 8 - Engine.

Feed Systems with liquid pressure accumulators (Fig. 7). ^{propellant} Liquid ^{propellant} pressure accumulators are small liquid ^{propellant} reaction engines from which propellant combustion products are fed into the propellant component tank where they are compressed and force the component into the main rocket engine.

If the propellant consists of two combustibles, then the power plant is provided with two liquid pressure accumulators, one for pressurizing the fuel and the other for the oxidizer.

The design of a liquid ^{propellant} pressure accumulator does substantially not differ from that of a conventional liquid-propellant reaction engine. Hence the propellant must somehow be fed into the pressure accumulator itself. This is achieved by forcing the propellant into the accumulator combustion chamber by means of compressed air from auxiliary tanks as in the case of the pressure feed systems. The combustion chambers of liquid-propellant pressure accumulators are attached to the top part of the main rocket propellant tanks.

Liquid pressure accumulators for fuel and oxidizers operate with the same propellant components but the ratio of these components is taken different depending on the purpose for which the pressure accumulator has been designed. Accordingly, the composition of gaseous combustion products expelled from the liquid pressure accumulator combustion chambers will also be different. As a rule, more oxidizer than necessary for the stoichiometric ratio is forced into the liquid pressure accumulator combustion chamber. The same is true in the case of fuel.

The possibility of obtaining in the pressure accumulator a gas with a different content of unexploited oxidizer or unburnt fuel represents one of the advantages of liquid-propellant accumulators

over powder accumulators which yield gases of identical composition both for pressurizing oxidizers and fuels. For this reason, with liquid-propellant pressure accumulators there is no danger of a chemical interaction arising between the gas pressurizing the component and the component itself.

Performance of the liquid-propellant pressure accumulator combustion chambers with a propellant component ratio far from optimal, i.e., operation with mixtures strongly enriched with oxidizers or fuels, is required also for another reason. Combustion of rocket propellants generates temperatures of about 3,000 to 3,500°C if the components are at a ratio at which there is just enough oxidizer to fully oxidize the fuel until it forms the final combustion products, carbon dioxide and water vapor. If gas at such temperatures is fed into the rocket propellant tanks, their walls will be strongly heated and may even burn out. By feeding into the liquid-propellant pressure accumulator combustion chamber a propellant mixture with an excess of one component, the temperature of the gaseous combustion products can be lowered to magnitudes representing no hazard for the material of which the propellant tank is made. Gas temperature in liquid-propellant pressure accumulators does usually not exceed 1,000 to 1,200°C.

A disadvantage of liquid-propellant pressure accumulators with respect to gas producing grain bottles consists in their relatively complex design and the difficulty of obtaining gases with specific parameters (pressure and temperature). Especially difficult to obtain are gases with constant temperature. Slight changes in the pressure at which the components are fed from the accumulator tanks into its combustion chamber lead to abrupt changes in gas

temperature.

As in the case of gas producing grain bottles, liquid-propellant pressure accumulators should be used in engines with low combustion chamber pressures.

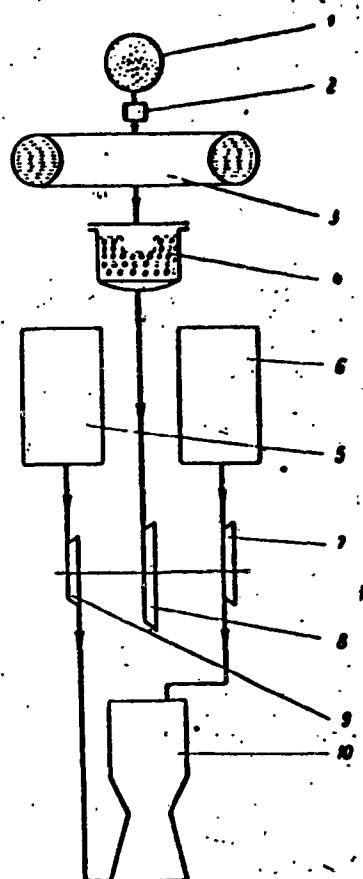


Fig. 8. Schematic of turbopump feed system

1 - High pressure gas tank; 2 - Pressure regulator; 3 - Hydrogen peroxide tank; 4 - Vapor/gas generator; 5 - Fuel gas; 6 - Oxidizer tank; 7 - oxidizer pump; 8 - turbine; 9 - fuel pump; 10 - engine

Pump feed systems (Fig. 8) differ substantially from gas pressure feed systems.

With this supply system propellants are not pressurized by gases into the combustion chamber but are forced into it by means of pumps driven by a special engine, the turbine. The entire assembly (pumps and turbine) is known as the turbopump unit. It is mounted between the propellant tanks and the rocket engine combustion chamber.

As a rule, the turbine wheel is on the same shaft with the working wheels of the fuel and oxidizer pumps. The turbine is driven by vapor/gas. The amount of propellant fed by the pumps is controlled by the number of turbine rotations. The pumps create feed pressure in the feed lines connecting the pump outlet with the engine inlet, whereas in the propellant tanks only a low pressure (about 2 to 4 kg/cm²) is maintained to improve the intake of propellant from the tanks by the pumps.

The turbopump feed system does not require especially solid and therefore heavy propellant tanks.

The vapor/gas driving the turbine is derived either from a special component which is not an engine propellant component, or from components used by the rocket engine. Hydrogen peroxide is frequently employed as a source of vapor/gas, obtained from decomposing hydrogen peroxide in vapor/gas generators by catalysts which are substances promoting decomposition.

The vapor/gas generator is a chamber containing the catalyst. Hydrogen peroxide is fed into it and it decomposes into water vapor and oxygen under liberation of heat. Liquid catalysts may

also be used for decomposing hydrogen peroxide, in which case the vapor/gas generator chamber becomes a mixing chamber for the liquid catalyst with hydrogen peroxide, and ^{for} the decomposition of the latter.

The vapor/gas thus formed has a temperature of about 450 to 500°. From the vapor/gas generator it is fed to the turbine which it drives and is then expelled into the air through special outlets.

By using as vapor/gas the generator gas obtained from the basic propellant components, the power plant design can be appreciably simplified. In this case the number of components to be carried by the rocket can be reduced, and an auxiliary propellant tank is no longer needed. Generator gas is produced by an assembly similar to the liquid-propellant pressure accumulator.

The temperature of the generator gas driving the turbine must not exceed 700 to 800°C since the turbine blades cannot withstand higher temperatures at which they fuse or lose their mechanical stability. To produce generator gas at low temperatures the propellant components are fed into the gas generator at a mixing ratio where one component considerably exceeds the other.

Chapter II

OXIDIZERS

Section 6. Liquid Oxygen

Liquid oxygen is a clear, bluish, highly mobile fluid. Boiling point at normal pressure is minus 183°C , temperature of solidification is minus 218°C . Critical temperature, i.e., the temperature above which oxygen can only be gaseous is minus 118°C . To critical temperature corresponds critical fluid pressure equal to 49.7 kg/cm^2 .

As an oxidizer of rocket propellants, liquid oxygen was first proposed by K. E. Tsiolkovskiy in 1903. It is one of the most powerful oxidizers because its molecule has no ballast atoms (as does nitrogen, and others). Due to this, propellants based on liquid oxygen are much more powerful and effective than ~~those~~ ^{and wiring} those based on other oxidizers ~~with the same fuel~~. Propellants with higher power factors are obtainable only with the aid of such oxidizers as ozone, elemental fluorine and fluorine monoxide which is a combination of oxygen and fluorine.

A conspicuous advantage of oxygen over other oxidizers is its low cost which, on the one hand, is due to the simplicity of its manufacturing technique and, on the other, to its unlimited availability. In fact, oxygen is one of the most widespread elements on earth. The overwhelming majority of compounds making up the earth's crust are combinations of various chemical elements with oxygen. The earth's crust contains about 49% oxygen. Water is made up of 88.9% oxygen.

In the water and oxygen-containing solids, oxygen is encountered in a chemically combined state, hence its derivation is associated with great technical difficulties and considerable energy output.

The atmosphere surrounding our planet also contains appreciable amounts of oxygen -- as an average, 20.93% by volume (23% by weight), the rest being taken up by nitrogen (78.3%) and other gases (1.04%).

Air oxygen is not chemically combined with other elements, hence its derivation requires no large energy output. Thus, the air is the fundamental source providing us with gaseous and liquid oxygen in large amounts. To obtain 1 m³ gaseous oxygen from the air requires only 0.5 to 0.6 kwh. The same amount of oxygen obtained from water by decomposing it with electric current requires 12 to 15 kwh.

Liquid oxygen was commercially produced long before it was used in rocket technology. Liquid and gaseous oxygen were applied on a large scale in a number of industry branches. It is used for welding and cutting metals, pig-iron smelting, steel founding, nonferrous metallurgy, in the chemical industry and in medicine. Large amounts of oxygen are used to convert low-quality solid fuels, such as lignite, peat and shales to highly valuable fuel gas.

Large-scale utilization of oxygen in various branches of industry as well as in everyday life has contributed to the development of the large oxygen-producing plants.

Production of Liquid Oxygen

As mentioned earlier, oxygen is chiefly taken from the air

where it is combined with other gases. To separate gaseous oxygen from the other gases of the atmosphere is a difficult process. It is much simpler to separate the gases of the air in a liquid state.

If air is cooled to a temperature of from -194 to -195°C it becomes a liquid consisting mainly of two liquid components (oxygen and nitrogen) and minor amounts of liquid argon, xenon and other gases. Table 1 gives the boiling points of substances being part of liquid air. We can clearly see that the boiling points of these fluids differ noticeably from each other. Liquid oxygen and nitrogen which account for the bulk of liquid air have boiling points differing from each other by some 13°C .

Table 1

Boiling Points of Air Components at Normal Pressure

Substance	Chemical formula	Boiling point, $^{\circ}\text{C}$
Nitrogen	N_2	-195.8
Oxygen	O_2	-182.95
Argon	Ar	-185.7
Neon	Ne	-245.9
Helium	He	-268.88
Krypton	Kr	-151.7
Xenon	X	-109.1
Oxygen	H_2	-254.4
Air		-192 -194

The process of cooling air to low temperatures, which corresponds to liquifying it, is based on the property of gases to cool off very strongly as they expand. An efficient and economic method of liquifying air was devised in 1939 by

the Soviet scientist P. I. Kapitsa. Fractionization of liquid air into oxygen and nitrogen is performed in so-called rectification columns.

Liquid oxygen used in rocket technology as a propellant oxidizer must have an optimum degree of purity. Any kind of impurity reduces the power factor of propellants based on it. Moreover, some admixtures may bring about difficulties in its storage, transport and application to rocket engines. Of the admixtures available in the air and whose presence in liquid oxygen is especially undesirable, dust, carbonates, acetylene and some other organic compounds should be cited.

One m^3 of air contains up to 0.01 g of solid particles (dust, soot, etc.). These solid particles may clog filters when filling the rocket with liquid oxygen. For this reason the air used by the plant for manufacturing liquid oxygen is thoroughly cleaned of all mechanical impurities.

Carbon dioxide is an indispensable component of the air. Its content ranges from 0.02 to 0.08% by volume. Maximum concentration of carbon dioxide in the air occurs in industrial districts, the lowest -- in rural areas.

At normal pressure carbon dioxide solidifies at a temperature of -78.5°C . Consequently, in liquid oxygen, at a temperature of -183°C at normal pressure, carbon dioxide must be in a solid state. Solid carbon dioxide (dry ice) has a certain solubility in liquid oxygen. In 1 liter of liquid oxygen no more than 3.6 cm^3 of carbon dioxide can be dissolved (converting to gaseous carbon dioxide taken at normal pressure). Carbon dioxide portions in excess of $3.6 \text{ cm}^3/\text{liter}$ are not fully soluble in liquid oxygen.

A part of it will precipitate in the form of a solid deposit.

The presence of solid dioxide in liquid oxygen may be the cause of the same complications during operation as those resulting from solid insoluble impurities, such as soot, dust and others.

Carbon dioxide in the form of solid particles is always present in liquid oxygen. Even filtering cannot totally eliminate it since during storage of liquid oxygen, because of its intensive vaportization, carbon dioxide will concentrate in it. There forms a supersaturated solution, i.e., a solution of carbon dioxide in liquid oxygen with a concentration in excess of $3.6 \text{ cm}^3/\text{liter}$, and the excess of carbon dioxide precipitates. Hence, when manufacturing liquid oxygen, appropriate measures are taken to reduce to a minimum the amount of carbon dioxide penetrating into it from the original raw material, atmospheric air.

Prior to liquefying the air from which the oxygen is taken, it is purified of carbon dioxide by passing it through an alkali solution (sodium hydroxide).

Purification of air from carbon dioxide is also effected by freezing the latter in special heat exchangers.

Organic gaseous substances, such as acetylene, ethylene and other gases may also be encountered in small amounts in the air. The presence of such substances in liquid oxygen is highly undesirable. Indeed, liquid oxygen forms with organic substances explosive mixtures of great destructive power, extremely sensitive to various influences from the outside (percussion, spark, etc.). Even the smallest amounts of organic impurities in liquid oxygen create the danger of forming explosive mixtures. This applies in particular to

acetylene. Air is purified of the latter by pumping it after liquification through silica gel filters. Acetylene remains on the silica gel surface.

Storage and Transport of Liquid Oxygen

The basic property of liquid oxygen which characterizes any operation with it, is its low temperature. It is known that many substances, both metallic and nonmetallic ones, abruptly change their mechanical properties when cooled to low temperatures. At liquid oxygen temperature, most metals considerably increase their ultimate tensile strength, decrease viscosity and become extremely brittle. Non-metals lose their elasticity at these temperatures. Rubber, for example, becomes as brittle as glass.

Fittings and containers for liquid oxygen may be made of such materials as copper and its alloys, aluminum and its alloys, and stainless steel. Ferrous metals are unsuitable for operations at low temperatures. Of the metals cited, aluminum and its alloys have the best properties. Stainless steel has a higher strength, but it is considerably heavier than aluminum. Aluminum alloys have a lower density and thermal capacity than steel and copper alloys, hence to cool the walls of aluminum containers to liquid oxygen temperatures less heat need be removed. This results in fewer losses of liquid oxygen when cooling aluminum containers prior to filling than this is the case when cooling steel or copper containers.

As gasketing material in oxygen pumps, valves and feed pipes, teflon may be used.

Organic substances soaked in liquid oxygen (oils, sawdust and wood shavings, rags, etc.) acquire explosive properties and a

high sensitivity to external influence. Hence, prior to filling the containers with liquid oxygen, all the feedlines and the containers themselves must be thoroughly cleaned and washed to remove all impurities and to scar the surfaces. Solvents such as chloroform, methylene chloride, trichloroethylene, and others, may be used for degreasing and cleaning oxygen containers.

Since liquid oxygen is continuously boiling, its long-lasting storage leads to considerable losses due to vaporization. Latent heat of vaporization of water is 10.55 times greater than that of liquid oxygen². Due to low heat of vaporization and to the enormous difference between ambient temperature and the temperature of liquid oxygen, its vaporization proceeds at an extremely intensive rate.

Liquid oxygen losses during storage can be reduced either by providing containers with good heat insulation warranting a minimum supply of heat to the oxygen outside, or by equipping the containers with devices by means of which to compress (condense) the oxygen vaporized and feed it back into the container. Storage of liquid oxygen in containers provided with return condensation devices will practically exclude oxygen vaporization losses.

Double walls provide fixed and mobile oxygen containers with good heat insulation. The space between the walls is either filled with heat-insulating materials with low thermal conductivity, or air is evacuated from it thus creating a heat-insulating vacuum jacket. Vacuum heat insulation yields the best results with regard to reducing liquid oxygen vaporization losses, but it is applicable only to low-capacity vessels since they are subjected to ambient air pressure. In large containers the space between

the inner and outer walls is filled with heat-insulating material.

The oxygen industry uses as heat-insulating materials such substances as slag wool, magnesium carbonate, glass wool, etc. Slag wool is used chiefly for the heat insulation of oxygen apparatuses employed in the production of liquid oxygen. Heat insulation of containers (tanks and reservoirs) uses mainly magnesium carbonate, a loose, white powder consisting of 55 to 60% MgCO_3 and 40 to 45% MgO . The heat-insulating properties of magnesium carbonate depend greatly upon its degree of moisture. With increasing moisture content its heat-insulating capacity drops, hence to insulate oxygen containers magnesium carbonate with a moisture content not exceeding 2.5% is used.

Liquid oxygen is stored and transported in tanks, being metal containers with ^a good heat-insulating layer attaining 300 to 350 cm and more in thickness. Tank capacity varies from 0.5 to 50,000 m^3 . Projects for reservoirs holding up to 1 million tons of oxygen are known. Their insulation must be about 10 m thick.

The magnitude of liquid oxygen vaporization losses during transport and storage depends on the size of the tanks. Losses in small-size tanks average about 0.3 to 0.35% per hour. The larger the tank, the smaller are oxygen losses due to vaporization. In large stationary reservoirs (several thousands of tons capacity) losses can be reduced to 0.6% per day.

Return condensation of oxygen vapors forming in the reservoir can be effected by means of so-called helium coolers. The reservoir's

top part (gaseous phase) is provided with coils through which liquid helium circulates continuously. The boiling point of liquid helium (-269°C) is considerably below that of liquid oxygen, hence oxygen vapors coming in contact with the helium-carrying pipes are strongly cooled and condense ; from the coil pipes the condensate flows back into the oxygen liquid phase. It should be noted that such a method for fighting liquid oxygen vaporization losses during transport or storage is quite costly.

To reduce the weight of rockets, oxygen tanks have, as a rule, no heat insulation. As a result, oxygen vaporization losses during filling may reach up to 50% of the filling weight. Such losses in already filled rockets are also considerable. Thus, in a 2.3 - ton aluminum tank without heat insulation vaporization losses amount to about 3% per hour. In tanks provided with vacuum jackets oxygen losses can be reduced to 0.5% per hour, but such tanks double their weight.

As soon as the oxygen tanks have been filled, the rocket must be immediately started. If start is delayed for some reason, the oxygen tank must be continuously filled up to compensate for the losses due to vaporization.

Liquid oxygen can be cooled to temperatures below its boiling point. Supercooled oxygen does not boil, hence until it is heated to the temperature ^{of} -183° its vaporization losses will be negligible. The time during which oxygen warms up to reach its boiling point depends on the degree of its supercooling. Thus, if a 2.3-ton rocket tank is filled with oxygen supercooled to a temperature of -193° , i.e., ten degrees below its boiling

point, the rocket may stand for 80 min without refilling the full oxygen tank.. During this period of time the oxygen in the tank will increase its temperature by 10° , whereupon intensive vaporization will start anew. Liquid oxygen can be supercooled by fluids with a lower boiling point (liquid nitrogen, boiling point -195° ; or liquid helium, boiling point -269°) pumped through coil pipes fitted in the liquid oxygen tank.

Supplying liquid oxygen to the working site involves repeated transfer from container to container. At the manufacturing plant liquid oxygen from stationary plant reservoirs is poured into mobile containers for shipment to the permanent storage site. From there it is taken to the launching site where it is filled into the rocket tanks. Liquid oxygen can be transferred from one container into the other by means of pumps or by pressurizing it with some gas. The most expedient one to create the required pressure is gaseous oxygen.

Pressure in the container from which liquid oxygen is being transferred can be created in the following two ways. First, by intensive vaporization brought about by heating the liquid oxygen in the container; second, a part of the liquid oxygen can be taken from the basic container into special heat exchangers where it is gasified, whereupon the gaseous oxygen is fed at an appropriate pressure into the liquid oxygen container. The second method requires no heating of the entire liquid oxygen mass but there arises the need for additional equipment in liquid oxygen reservoirs (heat exchangers, fittings, etc.) In the first method, the contact of gaseous oxygen having a certain excess pressure with liquid oxygen increases considerably the amount of gas bubbles

in the latter. These gas bubbles are undesirable since they lower the mean specific weight of liquid oxygen. Moreover, gas bubbles in liquid oxygen disrupt the normal operation of pumps feeding the propellant into the engine combustion chamber.

When forcing liquid oxygen out of large-size containers, a constant rate of transfer can only be ensured by special devices regulating the flow of compressed gas into the container being evacuated. This raises the production cost of reservoirs. This cost increases sharply as their size increases since in this case the containers must be built strong enough to withstand the pressure of compressed gas.

All of the above difficulties arising when transferring liquid oxygen from one container into another by pressurization are completely eliminated in the case of pump transfer systems. Centrifugal pumps ensure a rapid and reliable transfer of liquid oxygen. The pumps may be made of the same metals as liquid oxygen containers, that is, aluminum alloys, bronze and stainless steel.

Liquid oxygen is virtually non-toxic (non-poisonous). The oxygen vapors given off only refresh the atmosphere. Short contacts of liquid oxygen with unprotected parts of the body also entail no hazards, in fact, the gaseous oxygen layer formed prevents the skin from freezing. However, special care should be given to the fact that no combustible gases concentrate near liquid oxygen containers since their combination with oxygen vapors may result in the formation of explosive mixtures.

It should also be carefully avoided that the clothes of

the men operating with liquid oxygen not be soiled with oils or other organic substances since contact of liquid oxygen with such clothes may result in self-ignition and, hence, in traumas and catastrophes.

Propellants Based on Liquid Oxygen

Liquid oxygen used in rocket technology as an oxidizer must have a concentration of no less than 99% by volume. The remaining 1% is taken up by nitrogen and other admixtures.

The chief characteristic of propellants based on liquid oxygen as compared with other rocket propellants is their high calorific value and, as a consequence, the high temperatures generated in the combustion chamber of the engine. This high calorific value of oxygen propellants creates great difficulties in providing a reliable cooling of the engine.

Oxygen engines use as a coolant only one propellant component -- the fuel. Because of its low boiling point, the second component, liquid oxygen, is not yet used for cooling combustion chambers. Oxygen propellants have an oxidizer content 2.5 to 3 times that of the fuel (e.g., kerosene). Relatively small amounts of liquid are therefore required to cool the engine. Hence, in World War II liquid oxygen engines driving V-2 rockets used as a fuel component a mixture consisting of 75% ethyl alcohol and 25% water. This fuel has an appreciably lower calorific value than kerosene with oxygen, and forms a propellant with a relatively low combustion temperature. Moreover, the fuel-to-oxidizer ratio in such a propellant was considerably higher than in propellants using as a fuel pure alcohol, or, especially, kerosene compounds.

It should be noted, however, that even for the V-2, operating at a combustion chamber pressure of 16 kg/cm^2 , cooling was a serious problem. Modern rocket engines operate at combustion chamber pressures several times the one mentioned above. Increased combustion chamber pressure increases the efficiency of engine performance and reduces the weight of the power plant, but at the same time it increases the heat liberated per unit volume of combustion space.

The large amounts of heat liberated per unit volume of combustion space by rocket engines operating with oxygen propellants as well as other highly efficient propellants requires both inner and outer cooling of the engine. Inner cooling results in incomplete combustion of the fuel, in the engine chamber, that part of the fuel being ejected through the nozzle either in the form of vapor or as incomplete combustion products. This lowers the engine's efficiency manifested by a reduced specific impulse.

The propellant component used for inner cooling must have maximum thermal capacity and maximum latent heat of vaporization. Kerosene has a relatively low thermal capacity and low latent heat of vaporization, hence its rate of flow for cooling will be very high. At combustion chamber pressures exceeding a certain value, inner cooling of oxygen-oil rocket engines with fuel will therefore bring about such a strong drop in specific impulse that it is more expedient to use kerosene mixtures with fuels producing less heat but having better cooling properties than kerosene. Substitution of highly calorific fuels with low cooling power by fuels with somewhat lesser calorific value but higher cooling power permits the removal of considerable amounts

of heat already with external engine cooling. This heat is not lost for the engine but is returned with the component into the combustion chamber. Consequently, increased external cooling does not affect engine performance. Moreover, considerably less fuel will be required for inner cooling because of improved cooling power and because of an improved external cooling of the engine.

In particular, such a fuel mixture was used by the Americans to power the first stage of the "Vanguard" rocket which operated with the following propellant: oxidizer, liquid oxygen; fuel, a mixture of 95% gasoline, 4% ethyl alcohol and 1% silicone oil. The latter is introduced in the fuel to lubricate the propellant pump,

At the present time ^{the} difficulties in cooling liquid-propellant rocket engines operating with propellants of high heating value are being successfully overcome. This makes it possible to employ fuels with a high calorific value in liquid oxygen propellants.

The problem of cooling oxygen engines is somewhat simplified if as the fuel component we use substances with molecules having a higher content of hydrogen atoms. Hydrogen is one of the combustibles with the highest calorific value, but its combustion temperature in an oxygen atmosphere is considerably below that of other widely used fuels. Hydrogen burning in oxygen liberates an amount of heat equivalent to 3,210 kcal/kg at an ideal combustion temperature³ of 4,120°C, while oxycarbonic propellants have a calorific value of 2,130 kcal/kg at an ideal combustion temperature of 5,950°C.

Among the fuels with increased hydrogen content we cite, in the first place, elemental hydrogen, then such compounds as ammonia, hydrazine and its derivatives (methyl hydrazine, dimethyl hydrazine and others.). Liquid-oxygen propellants with such fuels have high specific impulse and develop during their combustion comparatively low combustion temperatures, thus facilitating the cooling of engines.

Section 7. Nitric-Acid Oxidizers

Nitric Acid

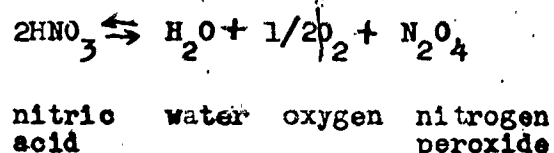
Oxidizers based on nitric acid are as widely used as liquid oxygen. The rapid adoption by rocket technology of these oxidizers is due, in particular, to the production of nitric acid (the basic component of nitric-acid oxidizers) on an industrial scale long before using it as an oxidizer of rocket propellants.

Nitric acid boils at a temperature of $+86^{\circ}\text{C}$ and freezes at -41°C . Thus, under normal conditions, it is a fluid. This is one of its advantages as a rocket propellant oxidizer over liquid oxygen. The comparatively low temperature of solidification and the high boiling point facilitate its storage, transport and transfer. Rockets powered by nitric-acid propellants can be kept for a considerable time filled with propellant components. This, as we have seen, has to be excluded in the case of oxygen.

Nitric acid, however, also has substantial operational drawbacks. It is expedient to use as rocket propellant oxidizer only

concentrated nitric acid containing no more than 3 to 4% water. But concentrated nitric acid has a low chemical stability, hence it decomposes during storage. Decomposition rate sharply increases with increasing temperature.

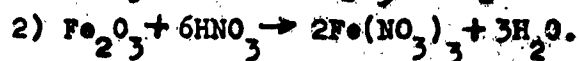
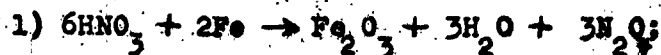
Decomposition of nitric acid by the following reaction



yields water, oxygen and nitrogen peroxide. As a result of chemical instability its properties as a rocket propellant oxidizer deteriorate on account of increasing content of water which, being an inert admixture, lowers the calorific value of the propellant. If concentrated nitric acid is stored in hermetically sealed containers, its decomposition increases the pressure in the container following liberation of gaseous oxygen (decomposition of 1 kilogram of nitric acid yields 87.5 liters gaseous oxygen). Hence the storing of nitric acid in hermetically sealed containers is connected with some hazards, especially in the summer.

But its main draw-back consists in its exceedingly high corrosive action, with respect to nearly any substance. This creates considerable difficulties in choosing the appropriate materials for feedlines and fittings as well as containers for protracted storage at bases and depots. Common rubber used as gasketing material in valves and pumps does not withstand the action of nitric acid, it either dissolves (it in) or coarsens and thus loses its packing properties. With metals,

concentrated nitric acid reacts in two stages. First it acts on the metal as an oxidizer reducing it to an oxide, and then the oxide reacts with nitric acid in the same fashion as do metal oxides with other acids:



This reaction with metals is precisely the reason for its exceptionally high corrosive action. . . Only noble metals (gold, platinum) are fully resistant to nitric acid. Technical metals, however, including stainless steels, aluminum and its alloys, are highly corroded by it. Of the plastics, teflon resists to nitric acid.

It should be noted that corrosion of metals in nitric acid is considerably increased when the acid is diluted with water. In fact, the acid is most corrosive when diluted with water to a concentration of 30 to 35%. Hence nitric acid containers must be thoroughly cleaned of acid residues since the acid draws water from the air and may therefore reach a concentration critical from the viewpoint of corrosion, and seriously damage the container.

Compared with liquid oxygen, operations with nitric acid are further complicated by the acid's toxicity. Contact with the human skin provokes painful ulcers which take a long time to heal. Therefore, if drops of nitric acid happen to hit the unprotected parts of the body, they must immediately ^{be} washed away with large amountsoof water or a 5% soda solution. Nitric acid vapors also have a very harmful effect on man. Their toxicity is 10 times that of carbon monoxide. Air containing 200 to 300 parts of nitric acid,

per 1 million parts of air irritates the skin and the eyes and destroys the lungs. Maximum permissible concentration of nitric acid vapors in the air where breathing is not dangerous yet, is 10 parts acid vapors per 1 million parts of air.

Propellants based on nitric acid have a considerably lower calorific value than oxygen-based propellants. Hence they have a lower specific impulse in the engine. Combustion of 1 kilogram of a mixture of nitric acid and kerosene at a stoichiometric ratio liberates about 1,450 kcal. Combustion of the same amount of an oxygen-oil propellant yields about 2,500 kcal.

Because of its low chemical stability and the low calorific value of propellants based on it, concentrated nitric acid has a limited use as a rocket propellant oxidizer. It is chiefly employed in compounds with nitrogen oxides.

Mixture of Nitric Acid with Nitric Oxides

Under specific conditions nitrogen reacts chemically with oxygen. Since nitrogen is an inert gas, its oxygen compounds are highly unstable. They easily react with combustibles and oxidize them.

Nitrogen forms with oxygen the following six compounds: nitrous oxide N_2O , nitric oxide NO , nitrogen dioxide NO_2 , nitrogen trioxide N_2O_3 , nitrogen peroxide N_2O_4 and nitrogen pentoxide N_2O_5 . Of these compounds only two can be used as rocket propellant oxidizers, NO_2 and N_2O_4 . The last oxides change easily into one another. At increased temperatures nitrogen peroxide almost entirely decomposes to nitrogen dioxide which has a dark brownish

color; with dropping temperature (0 to 5°C) there occurs an inverse process: nitrogen dioxide changes to nitrogen peroxide, a light yellow fluid.

Propellants based on nitric oxides have a considerably higher calorific value than those based on concentrated nitric acid. Thus, the calorific value of nitric oxide plus kerosene propellant exceeds that of nitric-acid propellants with the same fuel by 13.5%. Yet, application of nitric oxides as rocket propellant oxidizers runs into difficulties because of their working characteristics.

The chief drawback of nitric oxides is their high freezing point (-11°C) and low boiling point (22°C). However, they have turned out to be valuable in compounds with nitric acid, with which they form homogenous mixtures. These compounds have a number of advantages over nitric acid and pure nitric oxides from the viewpoint of both power and performance. Nitric oxides were found to be good means for chemically stabilizing nitric acid. With a content of 15 to 20% nitric oxides the acid virtually becomes chemically stable in a wide range of temperatures. Thus, there is eliminated one of the serious shortcomings of nitric acid, its chemical unstableness.

Nitric acid density is 1.51 kg/liter, that of nitric oxides -- 1.47 kg/liter. Compounds of nitric oxides and nitric acid have a density considerably greater than each of its components individually. Thus, a compound of 20% nitric oxides and 80% concentrated nitric acid has a density of about 1.63 kg/liter, 8% in excess of nitric acid, and about 11% in excess

of nitric oxides. The greater density of nitric acid and nitric oxide compounds as compared with the densities of the substances taken separately makes the compound more valuable as a rocket propellant component.

An increase in the density of a compound of two substances with respect to the density of each substance taken individually can only occur if in mixing these substances they interact with each other and form a new compound. In fact, nitric oxides as they dissolve in nitric acid react with the latter and form molecular compounds of the form $N_2O \cdot 2HNO_3$.

To evaluate the operational properties of rocket propellants the magnitude of their vapor pressure at ambient temperature is of great importance. The lower ^{the} vapor pressure of the component at temperatures to which it can be heated during storage, the more convenient it is in operation. Nitric oxides have a fairly high vapor pressure at ambient temperature (at a temperature of 50°C the vapor pressure of nitric oxides is 2,600 mm Hg). For this reason they are usually stored in carboys built to withstand high pressures. The nitric oxide and nitric acid compound must have a pressure higher than that of concentrated nitric acid. But since intermixing of these two substances yields not a simple mechanical mixture but a molecular compound, vapor tension in the mixtures does not rise proportionally to the increase of the easily boiling component (nitric oxide) contained in it but to a considerably lesser degree. Thus, in nitric acid containing 20% nitric oxides vapor pressure of the mixture at 20°C should be, were it a simple mechanical mixture, 215.2 mm Hg. Actually, however, it is 168 mm Hg. The relatively low pressure of saturated

vapors of nitric-acid oxidizers facilitates their storage and operation in rocket engines.

By adding nitric oxides to nitric acid, the boiling point is somewhat lowered. Thus, 20% nitric oxide solutions in nitric acid boil at a temperature of about 50°C, whereas pure nitric acid boils only at 86°C. Lowering of the oxidizer boiling point deteriorates its operational properties, but at the same time nitric oxides considerably lower the temperature of solidification of the oxidizer, ^{and this} appreciably improves its operational characteristics. The temperature at which solid particles precipitate from a mixture of nitric acid with 20% nitric oxides is -70°C, whereas concentrated nitric acid freezes at a temperature of -41°C.

The power factors of propellants based on nitric-acid oxidizers are also higher than those of propellants based on concentrated nitric acid. The calorific value of the propellant and, hence, specific impulse increase in proportion with an increasing nitric oxide content in the oxidizer. Hence, from the viewpoint of improving the propellant power factors, it is desirable to have nitric-acid oxidizers with a maximum percentage of nitric oxides. Yet, a high content of the latter improves the oxidizer power factors, on the one hand, and deteriorates some operational characteristics (lower boiling point, increased vapor tension, etc.) on the other. In practice, therefore, mixtures are used in which nitric oxide content does not exceed 25 to 30%. Nitric-acid oxidizers used in the USA contain 4, 12 and 22% nitric oxides.

Toxicity of nitric oxides is about the same as that of nitric acid, but because of greater volatility of the former, they increase the hazard in handling nitric-acid oxidizers.

Corrosive power of anhydrous nitric acids is considerably lower than that of nitric acid. But their admixture to nitric acid, though it does not increase the corrosive power of the latter, does virtually not reduce it. The chief shortcoming of nitric acid as ^arocket propellant oxidizer, its high corrosive power with respect to all construction materials, remains unchanged also when using oxidizers containing a high percentage of nitric oxides.

Protection of Metals Against the Corrosive Action of Nitric-Acid Oxidizers

It was said earlier that the chief drawback of oxidizers based on nitric acid is their corrosive action. This fact causes considerable inconveniences in storing them or using them in rocket engines.

Attempts to protect the metal against the oxidizer's destructive action by coating its inner surfaces were unsuccessful. Even the slightest flaw in the protective coating through which the oxidizer can contact a small metal section of the container wall leads to a fast destruction of that section. The application of high-quality coatings to the entire metal surface to be protected against the action of the liquid and gaseous phase of the oxidizer turned out to be an extremely complex endeavor.

An effective means to reduce the rate of corrosion of the metals in nitric-acid oxidizers are special additives known as inhibitors.

For nitric acid and oxidizers based on it, sulfuric acid H_2SO_4 can be used although the latter is of itself quite aggressive with respect to metals. Nonetheless, mixtures of nitric and sulfuric acid have a considerably lower corrosive action than each acid taken separately.

This fact can be explained as follows: sulfuric acid reaction with the metal of the container wall forms a sulfate. If the container is made of ferrous metal, iron sulfate Fe_2SO_4 is formed; accordingly, aluminum containers yield aluminum sulfate $Al_2(SO_4)_3$, etc. Sulfates are weakly soluble in nitric acid and its mixtures with nitric oxides. The reaction yielding sulfates takes place directly on the container walls. Because of their low solubility in nitric acid and nitric-acid oxidizers, these sulfates remain on the container walls as some sort of a protective film preventing direct contact between the metal wall and the nitric-acid oxidizer. As a corrosion inhibitor for nitric-acid oxidizers, sulfuric acid is effective only if its content in the oxidizer exceeds 5 to 10%.

While the admixture of sulfuric acid to the nitric-acid oxidizer reduces its corrosive action, it also impairs other properties of the oxidizer. Sulfuric acid is no oxidizer (its molecule lacks active oxygen since all the oxygen atoms are bound with "combustible" sulfur and hydrogen atoms), hence its presence in nitric-acid oxidizers leads to an inadmissible reduction of the latter's power parameters.

Having a boiling point ($336^{\circ}C$) higher than that of nitric acid, sulfuric acid is almost non-volatile, hence mixed with a

nitric-acid oxidizer it does virtually not enter into the oxidizer vapors. Its effect as a corrosion inhibitor is therefore confined only to the fluid, whereas corrosion rate of container walls exposed to the action of oxidizer vapors remains as high as with oxidizers without sulfuric acid.

In nitric-acid oxidizers, sulfuric acid yields large amounts of precipitates, metal sulfates (of the metal of which the container is made) difficultly soluble in the oxidizer. The accumulation of these deposits may result in an obstruction of feedlines and valves during the transfer of the oxidizer, the filling of rocket tanks and, most important of all, during engine performance in flight. Small deposit particles which have gone through the filter during the filling of the rocket with oxidizer, or which have formed in the oxidizer tank itself, may clog the engine's manifolds.

Orthophosphoric acid H_3PO_4 is another additive which reduces corrosion rate of metals in nitric-acid oxidizers. The protective action of this acid manifests itself with concentrations in the oxidizer considerably weaker than those of sulfuric acid. In fact, only about 1% of this acid need be added to the oxidizer. Like sulfuric acid, orthophosphoric acid is an inert constituent of the oxidizer since its molecule lacks active oxidizer atoms (oxygen) or active fuel atoms. The power factors of oxidizers inhibited with orthophosphoric acid are less impaired than those inhibited with sulfuric acid since the latter must be added to the oxidizer in portions 5 to 10 times greater than those of orthophosphoric acid. which, however, has nearly all the short-

comings of sulfuric acid, such as formation of deposits in the oxidizer, absence of an inhibiting action in the gaseous phase, and others.

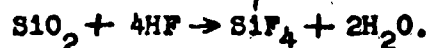
The corrosive action of nitric-acid oxidizers is strongly reduced by hydrogen fluoride HF. Under normal circumstances this is a highly toxic gas, well soluble in water. Added at a rate of 0.5 to 1.0% to the nitric-acid oxidizer, it sharply reduces its corrosive action against aluminum and its alloys. A thin and extremely resistant film of aluminum fluoride AlF_3 forms on the walls of aluminum containers. This film is an excellent protection of the metal against the corrosive action of nitric-acid oxidizers. Hydrogen fluoride has a fairly low boiling point ($20^{\circ}C$), hence it is present as a gas in amounts sufficient to form the protective film on that portion of the container surface which is not washed by the fluid. This property gives it a great advantage over such inhibitors as orthophosphoric and sulfuric acid.

Since hydrogen fluoride protects aluminum and its alloys against corrosion not only as a fluid but also as a vapor, no deposits are formed in nitric-acid oxidizers inhibited by this substance during extended storage in aluminum or aluminum-alloy containers.

Contact of glass parts (e.g., measuring tubes of containers) or materials containing a high percentage of silicon, with nitric-acid oxidizers containing 0.5 to 0.7% hydrogen fluoride must not be permitted, since it reacts with

silicon (glass has a high content

of silicon dioxide) in the following fashion:



Silicon fluoride formed here volatilizes since at ambient temperature it is a gas. The reaction between hydrogen fluoride and silicon-carrying substances continues until one of the components participating in this reaction has not been completely exhausted.

There exist, in addition to those mentioned, also other additives which reduce corrosion rate of metals in nitric-acid oxidizers.

Propellants Based on Nitric-Acid Oxidizers

Two types of propellants exist in this class: anergolic and hypergolic.

Nitric acid is a chemically active substance which at normal temperature reacts with most organic and inorganic combustibles. The heat liberated by this reaction causes self ignition of mixtures of nitric acid with certain fuels.

Not all the fuels igniting on contact with nitric-acid oxidizers can be used as components for hypergolic rocket propellants. Practice shows that the only suitable ones are fuels igniting no later than 0.03 sec after mixing with the oxidizer. With greater ignition delay time the fuel can no longer be used as a hypergolic in liquid propellant reactive engines, which must then be started with special ignitors.

The requirement that hypergolic propellants have an ignition delay no longer than 0.03 sec is dictated by the peculiar charac-

teristic of starting reactive engines. No special ignition devices are provided for the start of engines with hypergolic propellants. The components (fuel and oxidizer) are admitted to the chamber where they come in contact with each other and produce ignition which marks the beginning of engine performance. If the time required for the ignition of the propellant after mixing exceeds 0.03 sec, large amounts of propellant accumulate in the engine chamber.

Upon ignition, pressure in the chamber rises abruptly. This may lead to knocks or even to the explosion of the engine.

Amines may be used as hypergolic propellant components. As a rule, however, they ignite spontaneously with nitric-acid oxidizers with an ignition delay period exceeding 0.03 sec. On the other hand, mixtures of two or several amines have, for the most part, an ignition delay period shorter than any of them taken separately. Widely known is a fuel called "tonka" (German name) which, with nitric acid and its compounds with nitric oxides, forms a hypergolic propellant. "Tonka" is a mixture of two amines, triethyl amine and xylidine. Its ignition delay period after mixing with nitric-acid oxidizers does not exceed 0.03 sec even if the temperature of the components is lowered to -40°C .

Besides amines, some other substances can also form hypergolic propellants with nitric-acid oxidizers. Fuels such as hydrogen and its derivatives, in particular unsymmetrical dimethyl hydrazine, are spontaneously ignited with these oxidizers with particular ease. Ignition delay period of dimethyl hydrazine mixed with nitric acid

is one-tenth of that mixed with "tonka".

Studies are being conducted in the USA with mixtures of dimethyl hydrazine and hydrocarbon fuels (of the aircraft fuel type JP-4). These mixtures are spontaneously ignited on contact with nitric-acid oxidizers with an ignition delay period permissible for reactive engine operation.

Ignition delay period of hypergolic nitric-acid fuels depends to a great extent upon the temperature of components and water content of the oxidizer. A drop in component temperature and an increase in oxidizer water content results in an increased ignition delay period. By increasing the chemical activity of their components, the ignition delay period of hypergolic propellants can be reduced. There is known a series of additives to nitric-acid oxidizers and fuels which reduce that period. These are sulfuric acid H_2SO_4 , ferric chloride $FeCl_3$, iron nitrate $Fe(NO_3)_3$, and copper salts can be added for this purpose to nitric acid and oxidizers based on it. Ignition delay period is strongly reduced and combustion rate of propellants based on nitric acid is strongly increased by permanganates which are powerful oxidizers.

While hypergolic propellants facilitate the starting of engines and somewhat simplify their design, they complicate the operation of rockets. Spilling during rocket filling or leaks in the feedlines of the power plant may easily lead to fires. Hence operations with hypergolic propellants must be performed under especially careful safeguards to prevent their components from mixing accidentally.

With nitric-acid oxidizers, fuels not forming hypergolic propellants may be used. Such are, e.g., petroleum products.

for the start of engines operating with such propellants, special priming fuels are required. Fuels igniting spontaneously with nitric acid, such as, e.g., "tonka", may be used as igniters. The fuel component igniting spontaneously with nitric-acid oxidizers is filled into the rocket in amounts required only to produce the ignition torch in the combustion chamber.

The cooling of engines powered by nitric-acid propellants does not encounter the difficulties mentioned in discussing propellants on the base of liquid oxygen. The former have a lower calorific value than the latter (e.g., kerosene produces with oxygen a propellant with a calorific value 1.8 times that of the one formed with an nitric-acid oxydizer). As a result, a heat flow of lesser magnitude is transferred through the combustion chamber walls. Nitric-acid propellant engines can be cooled with fuel, oxidizer and, with both components simultaneously, if separate pockets for the fuel and the oxydizer are provided in the jacket space. Thus, large amounts of coolant are available for external cooling in nitric-acid propellant engines.

Nitric acid and its mixtures with nitric oxides have a good cooling power. Because of the comparatively small amount of heat liberated per unit volume of combustion space in medium and large-size nitric-acid propellant engines, however, they can only be cooled with fuel irrespective of the fact that the amount of oxidizer filled into the rocket is 3.5 to 4 times that of fuel. Small engines of the type above with a thrust of about 1 to 3 tons cannot be sufficiently effectively cooled with fuel alone. For this reason oxidizer is used as a coolant.

Section.8.. Hydrogen Peroxide

Hydrogen peroxide H_2O_2 has been manufactured commercially for over 70 years. Its easy decomposition by the action of various kinds of impurities was responsible for its production as a 35% solution in water. Production of stronger concentrates began only shortly before World War II in connection with the development of rocket technology. England and the USA have recently been producing 90 and 99.7% hydrogen peroxide. 99.7% concentration.

Most widespread in rocket technology are aqueous hydrogen peroxide solutions of 80 and 90% strength. Safe handling of concentrates of such strength could be warranted by adding to them special substances called stabilizers. The chemical stability of hydrogen peroxide can be sharply increased by adding to it phosphoric, acetic or oxalic acid, hydroxyquinoline, etc. An indispensable condition for chemically stabilizing hydrogen peroxide is also its purity. Negligible impurities bring about its decomposition.

Hydrogen peroxide (100% strength) is a clear liquid, solidifying at a temperature of $1.7^{\circ}C$ and boiling (with decomposition) at a temperature of $150^{\circ}C$. It mixes with water at any ratio. If diluted with water, its temperature of solidification drops. Thus, an 80% solution in water solidifies at a temperature of $-22^{\circ}C$. Hydrogen peroxide makes it possible to obtain oxidizers with even lower temperatures of solidification. A mixture consisting of 6% water, 40% ammonia nitrate NH_4NO_3 and 54% hydrogen peroxide has a temperature of solidification of $-40^{\circ}C$. A characteristic feature of hydrogen peroxide and its

aqueous solutions is a tendency to supercooling. In fact, it may be supercooled to 20 to 30°C below solidification temperature and still remain in a liquid state for a long period of time.

Hydrogen peroxide is obtained by absorbing heat from the surrounding medium. Conversely, it liberates heat as it decomposes. Hence its low chemical stability.

Stability of hydrogen peroxide decreases as its concentration increases. However, the compound always decomposes to some degree, whatever the storage conditions. Decomposition rate especially increases as the temperature rises. Some substances, such as copper and its alloys, lead, and others, accelerate the decomposition process of the peroxide. Other materials, such as carbon and stainless steel, also accelerate the decomposition of the compound although at a lower rate than copper and lead. The decomposition of the peroxide in contact with metals and non-metals depends not only on their chemical composition but also on the condition of their surfaces. Scratches, burrs and defects cause hydrogen peroxide to decompose at an accelerated rate.

The material best suited for apparatus operating with hydrogen peroxide is pure aluminum. As packing materials, teflon, fully halogenated polyethylene and (at moderate temperatures) polyethylene can be used.

Prior to filling, containers undergo a special treatment (passivation) to remove any impurity which could accelerate the decomposition of the compound. After this treatment the container is rinsed with a weak solution of hydrogen peroxide.

Even if stabilized with special admixtures, hydrogen peroxide decomposes continuously and liberates gaseous oxygen. In the

case of storage in hermetically sealed containers, pressure within may therefore build up to dangerous levels. For this reason the containers are provided with safety valves which operate as soon as pressure within the container rises beyond the permissible level. In designing fittings, feedlines and containers for the peroxide, units where it could stagnate or impurities such as corrosion products could accumulate are carefully avoided. Such impurities may cause the hydrogen peroxide to explode.

Although the corrosive action of hydrogen peroxide is weak compared with that of nitric acid, some materials are noticeably corroded by it. Corrosion is especially strong at the joints between different metals in contact with the peroxide. In this case there forms an electrochemical pair to eliminate which the metals in the peroxide are connected with plastic lining. This eliminates electrochemical dissolving of the metal.

Hydrogen peroxide is explosive and inflammable, the latter property being due to its high oxidizing power. Many organic substances (fabric, paper, oils) burn on contact with concentrated hydrogen peroxide. It is stored in places away from dwellings and other buildings. Reservoirs must be kept clean, storage of combustible materials in them is inadmissible.

The explosiveness of the liquid is due to its continuous decomposition with liberation of gaseous oxygen and also to the fact that its vapor may readily explode if acted upon from the outside. Decomposition rate increases with rising temperature, and the decomposition process itself releases heat. Thus, the rate of decomposition reaction initiated by some impurity may, because of heating, attain dangerous magnitudes after some time.

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At 175°C liquid hydrogen peroxide decomposes instantly, i.e., the decomposition process becomes explosive. Hence, when raising the temperature of hydrogen peroxide above ambient temperature by 5 to 10°C, an additional amount of stabilizer must be added to it in order to reduce the intensity of decomposition. Should this not stop further evolution of heat, water should be added. Hydrogen peroxide diluted to 50% becomes completely explosion-proof.

Liquid hydrogen peroxide has a low sensitivity to impact and blasts. At ambient temperature (20 to 25°C) a concentrate up to 99% does not explode from the effect of a primer.

Under service conditions explosions may happen in using hydrogen peroxide in the engine when blasts occur in the combustion chamber. The blast wave may bring about an explosive decomposition of the peroxide in the feedlines which may spread to the peroxide tanks.

Hydrogen peroxide vapors are considerably more explosive than the liquid.

Explosion of saturated vapors of water dilutes of hydrogen peroxide from external stimulation (sparks, heating, impact, etc.) occurs if the vapor contains 30 to 40% peroxide. Such a concentration in vapors from 80 to 85% liquid peroxide is possible only if the latter is heated up to 120 to 125°C. Such temperatures under storage and transport conditions are seldom attained. However, a great explosion hazard may arise in the case of fire of the reservoir when the liquid is heated to dangerous temperatures.

Fuels Based on Hydrogen Peroxide

Since a hydrogen peroxide molecule contains a large amount of

active oxygen, the peroxide may be used as an oxidizer of combustibles. Moreover, decomposition releases heat energy which may be converted to work. Hydrogen peroxide may therefore be used also as an oxidizer of bipropellants or, by itself, as a monopropellant.

Table 2

Power Parameters of Some Propellants
Fuel: Kerosene, $p_k = 20 \text{ kg/cm}^2$, $p_{ex} = 1 \text{ kg/cm}^2$

Oxidizer	Oxidizer-to-fuel weight ratio	Specific weight of fuel mixture	Combustion temperature °C	Specific impulse kg sec/kg
Liquid oxygen	2.25	1.02	3000	250
85% hydrogen peroxide	8.5	1.28	2300	230
Nitric acid	5.0	1.4	2600	230

We see from the table that in terms of specific impulse fuels based on hydrogen peroxide are not inferior to nitric-acid fuels while having a considerably lower combustion temperature. In fact, their comparatively low combustion temperature is their great advantage over other fuels. Another positive aspect of hydrogen peroxide is its relatively high density, which is higher than the density of oxygen fuels but lower than that of nitric-acid ones.

Because of its low corrosive action and volatility, hydrogen peroxide is simpler to store over long periods of time in rocket tanks than is nitric acid or liquid oxygen. This is of paramount

importance in the operation of rockets which must be ready to launch at any time.

The fact that hydrogen peroxide decomposes in the presence of catalysts permits to have engines operating with that oxidizer without a special start igniter. Instead, the engine can be started by so-called thermal starting. Hydrogen peroxide is fed into a precombustion chamber (a small space connected with the main combustion chamber), where, reacting with a catalyst, it decomposes. The hot gaseous decomposition products are fed into the main combustion chamber into which, after building up in it pressure required for normal fuel combustion, fuel is injected.

Thermal igniting is less dangerous than any other form of ignition of rocket engines (pyrotechnical, chemical, electric spark, etc.).

Starting of the rocket engine is the most dangerous operation stage which frequently ends up in the explosion of the engine itself. Explosions may occur not only in the case of premature ignition, as mentioned earlier, but also in the case of malfunctioning fuel or oxidizer cutoff valves. If these valves are not tight, propellant components flow into the combustion chamber prior to starting and accumulate there. At start, pressure sharply increases and the engine explodes.

In the case of thermal ignition, instead, the gaseous decomposition products of the peroxide admitted from the relatively small precombustion chamber to the main combustion chamber expell from the latter any fuel which may have accumulated there at start.

Thus an explosion of the combustion chamber becomes virtually impossible. Safe rocket engine starting is of particular importance for manned vehicles.

Hydrogen peroxide forms an anergolic fuel with alcohols and kerosene, and a hypergolic - and with hydrogen and hydrazine hydrate. In World War II, German air interceptors were powered with a fuel consisting of hydrazine hydrate + hydrogen peroxide.

The latter is no longer used as an oxidizer of rocket propellants at the present time, since with peroxide concentrations of 80 to 85% strength these propellants are considerably less powerful than those based on oxygen and nitric acid with nitric oxides. However, once operations with 100% hydrogen peroxide will become technically possible, its application as a component of the basic propellant is not to be excluded. Computations show that propellants based on 100% hydrogen peroxide are not inferior, as regards density, to propellants based on nitric-acid oxidizers (nitric acid + 22% nitric oxides) and excell them by 7 to 9 kg sec/kg specific impulse.

Hydrogen peroxide is widely used to obtain vapor/gas for turbopump feed systems of rocket engines. Propellants for the operation of TPU have the following specifications: sufficiently high power factors to ensure with ^a minimum rate of flow the operation of pumps; a relatively low combustion temperature. Most widespread in use as a monopropellant driving turbopump units is 80 to 85% hydrogen peroxide. Decomposition of 80% peroxide liberates vapor/gas at a temperature of 450 to 500°C. Besides hydrogen peroxide, a catalyst is used to obtain vapor/gas. Decomposition

of one kilogram of peroxide requires 0.05 kg of liquid catalyst consisting of a 35% alcohol solution of NaMnO_4 (sodium permanganate).

Maximum temperature permitted for the safety of turbines is 1.5 times higher than decomposition temperature of a hydrogen peroxide solution of 80% strength. Hence, to economize peroxide consumption, aqueous solutions of 90% strength are now being used in England and the USA. These solutions have a higher decomposition temperature and, consequently, a higher energy content per unit of weight.

The power factors of monopropellants based on hydrogen peroxide can also be increased by preparing mixtures containing, in addition to peroxide and water, such fuel components as ethyl alcohol, glycerine, acetone, and others. Thus, by introducing 8% ethyl alcohol in a 50% aqueous solution of hydrogen peroxide, we can obtain a monopropellant with a combustion temperature near 800°C . Such a mixture is more powerful than hydrogen peroxide of 80% strength and is safer to handle.

Section 9. Oxidizers of the Future

Liquid Ozone

At normal temperature ozone, O_3 , is a bluish gas 1.6 times heavier than air. At -112°C and a pressure of 1 kg/cm^3 ozone becomes a dark blue liquid. It solidifies at -250°C . Latent heat of vaporization is 47 calories per kilogram mole. Of all the possible rocket propellant oxidizers, liquid ozone is the

most powerful one. Like oxygen molecules, an ozone molecule consists of oxygen atoms alone. Nevertheless, ozone and oxygen have different chemical and physical properties, hence propellants based on them have different power factors. The higher power factors of ozone with respect to oxygen are due to two reasons: first, ozone forms in conjunction with heat absorption, i.e., it is an endothermic compound; secondly, liquid ozone has an appreciably higher density than liquid oxygen.

Since in the formation of 1 kg ozone from oxygen about 720 kcal are absorbed, the same amount of heat is liberated when it decomposes into oxygen atoms. This means that when a fuel is burned in ozone, heat is liberated not only by the reaction of fuel atoms combining with those of the oxidizer but also as a result of the decomposition of the molecules of the oxidizer, ozone. As a result, ozone forms with the fuel a propellant with a calorific value 23 to 24% higher than that of oxygen.

Among rocket propellant oxidizers, ozone is the least used one today. The difficulty of producing ozone and applying it to rocket technology is due to its excessively high explosiveness.

The nature of the explosive decomposition of ozone remains unexplained to this day. Apparently it is either connected with the endothermic nature of this compound or its sensitivity to the catalyzing action of negligible amounts of admixtures or else a combination of these two factors. There exist in the literature many contradictory views on this subject.

Comprehensive investigations into the chemical stability of ozone have been conducted in the USA in recent years. A number of authors whose works were published abroad claim that they succeeded

in finding the cause for ^{the} instability of liquid ozone. It is said to be the catalyzing effect of negligible organic admixtures, present in ozone, on the decomposition process. One American author even describes a method for obtaining stable ozone. Oxygen, the mother gas of ozone, is to be purified of organic impurities by passing it at 720°C over copper oxide which, under these conditions, fully oxidizes to carbon dioxide all organic impurities contained in oxygen. Subsequent tests have shown, however, that such ozone still exploded from the smallest stimulation. Thus, there are as yet no directions in the literature as to the utilization of liquid 100% ozone as an oxidizer. However, ozone as a component of compound oxidizers is of conspicuous interest.

At the boiling point of liquid oxygen (-183°C) ozone dissolves in oxygen forming a homogeneous mixture. Ozone solutions in liquid oxygen up to a strength of 25% are fully stable and nearly insensitive to outside stimulation. Solutions of such strength can be safely transported and used in rocket engines.

The power factors of ozone solutions in liquid oxygen exceed those of pure oxygen. The calorific value of propellants based on ozone-oxygen oxidizers (25% solution) exceeds that of oxygen-base propellants by some 5%. Moreover, introduction of that amount of ozone in liquid oxygen increases the oxidizer's density by 12.5%. These advantages of ozone-oxygen oxidizers over pure oxygen may play a decisive role, all other conditions being equal, in the attempt to increase the range of rockets.

Ozone is chemically more active than oxygen, this being due to the particular structure of its molecules. A number of fuels, including unsaturated hydrocarbons, may ignite spontaneously on contact with ozone or a mixture of ozone and liquid oxygen. Ignition

delay for such hypergolic propellants does not exceed the permissible time, i.e., 0.3 sec.

Due to the chemical activity of ozone, small amounts of it (3 to 5%) in oxygen accelerate combustion of the propellant in the engine combustion chamber. An increased burning rate of the propellant permits to reduce its stay time in the combustion chamber, i.e., it permits to reduce the size of the combustion chamber and, hence, build lighter and more compact engines.

Despite the above advantages of ozone-oxygen mixtures over pure oxygen, they are not being applied in rocket technology as yet. This is due to difficulties arising in the operation with such mixtures. The boiling point of ozone (-112°C) is considerably higher than that of oxygen (-183°C). Hence during protracted storage of ozone-oxygen mixtures, oxygen will evaporate first while the ozone content of the mixture will increase in time. At -183°C up to 25% liquid ozone may dissolve in liquid oxygen. With a higher ozone content, demixing takes place. The bottom layer with a higher density represents a solution of 55% ozone in oxygen, and the top one a 25% ozone solution. Ozone solutions in liquid oxygen with a strength in excess of 55% are again homogeneous and do not demix at -183°C and a pressure of 1 kg.cm^2 but, like pure ozone, they are highly explosive.

Although no efficient means have been found to this day for reducing the sensitivity of ozone and its concentrates in liquid oxygen to outside stimulation, the high power of rocket propellants based on liquid ozone induces the Americans to continue the investigations for its stabilization.

Ozone is highly toxic. Amounts of 0.00002% by volume can be detected in the air by its characteristic odor. Concentrations of 0.03% by volume strongly irritate the respiratory system and the eyes. A stay of 2 hours in an atmosphere containing ozone in a concentration of 0.04 to 1.0% by volume is fatal to man. By American data, the maximum permissible ozone concentration in the air is 0.0001 to 0.00001% by volume. Its toxicity exceeds that of such a strongly poisonous substance as nitric acid by tens of times.

Fluorine Oxidizers

The general advantage of fluorine oxidizers over oxygen-base oxidizers is their high chemical activity and high density. This applies to both oxidizers and propellants based on them.

Among the fluorine compounds of interest as rocket propellant oxidizers we cite elemental fluorine F_2 , nitrogen trifluoride NF_3 , fluorine monoxide OF_2 , chlorine trifluoride ClF_3 and bromine pentafluorine BrF_5 .

Among all the fluorine oxidizers the most powerful one is elemental fluorine, while bromine pentafluoride has the greatest density. In rockets with small-size propellant tanks the latter may be the most suitable oxidizer.

Liquid Fluorine

Until 1940 elemental fluorine was never practically applied. Produced in very small amounts in the laboratory it was chiefly used in research. But with the development of atomic industry

there was an increasing demand for uranium hexafluoride for the production of which elemental fluorine was required. This led to the search of commercial methods for obtaining fluoride and to the study of its properties.

At the present time fluorine is produced on a commercial scale in the USA. The main raw material for its production is fluorite CaF_2 from which potassium fluoride and hydrogen fluoride are produced. From the mixture of the latter two, fluorine is obtained by electrolysis.

It was held until recently that elemental fluorine will hardly ever be used as an oxidizer for rocket propellants. There were various reasons for this view.

It is known that fluorine is chemically the most active element which reacts with nearly all the substances at ambient temperature. It was believed that this would make it extremely difficult to choose the appropriate materials for apparatus and containers. For the same reason fluorine was regarded as the most toxic substance the handling of which will be complex and dangerous. The main reason, however, was that until recently fluorine was held to have a low density.

The density of liquid fluorine at boiling point was determined as early as 1897 and was taken to be equal to 1.1 kg/liter, i.e., less than the density of liquid oxygen (1.14 kg/liter) and considerably less than that of liquid fluorine monoxide (1.52 kg/liter). A thorough check conducted by the California Institute of Technology (USA) in 1952 showed that the density of liquid fluorine at boiling point is 1.51 kg/liter, i.e., that it is greater than the density

of liquid oxygen and close to that of fluorine monoxide. From that moment the interest for liquid fluorine as a rocket propellant oxidizer sharply increased.

Until normal conditions fluorine is a yellow-green gas, which liquifies at a pressure 1 kg/cm² and a temperature of -188.18°C. It solidifies at -219°C.

Of all the known chemical elements, fluorine has the most powerful oxidizing action. It combines with virtually all elements and oxidizes them. Even such an element as oxygen, which is an extremely powerful oxidizer, is oxidized by fluorine. It burns in a fluorine atmosphere. It was held until recently that such inert gases as argon, xenon, neon and others are incapable of reacting with other substances. It was found, however, that under specific conditions fluorine may react even with these gases.

This powerful chemical activity creates specific difficulties in using fluorine. The overwhelming majority of materials does not withstand contact with liquid fluorine and reacts with it. But since several metals form during this reaction a fluorine-resistant film of fluorides firmly connected with the surface of the metal and protecting the latter against the action of fluorine, the problem of fighting its corrosive action was found to be fully solvable.

The resistance of metals to fluorine is determined by the firmness of the connection between the fluoride film and the metal itself. Such metals as nickel, stainless steel, Monel metal, brass, copper and aluminum ^{are suitable} materials for fittings and containers of liquid and gaseous fluorine if the latter is stored at temperatures no higher than room temperature. At higher temperatures, gaseous

fluorine is better stored in Monel metal containers since it has the best resistance to the action of both gaseous and liquid fluorine.

As packing materials, copper, aluminum and plastics such as teflon can be used. It should be noted that teflon and metals can be fluorine-resistant only if the following two requirements are fulfilled: First, the surface in contact with fluorine must be thoroughly cleaned of all impurities; secondly, the material must not be exposed to the action of a fluorine flow flowing at a high velocity.

Any organic impurities in fluorine act as initiators of the combustion process. Ignition of impurities in fluorine leads also to the ignition of the container or feed line material. Hence equipment operating with both liquid and gaseous fluorine must be scoured, cleaned of all sorts of impurities and dried. Thereafter the equipment is treated with gaseous fluorine diluted with an inert gas. The concentration of gaseous fluorine in the inert gas is chosen such that it is sufficient to ignite and burn all impurities which remain on the surfaces of equipment after its preliminary cleaning, but not strong enough to ignite the material of which the equipment is made.

As the metal surfaces are treated with gaseous fluorine there forms, along with the cleaning of the surface, a fluoride film which protects the metal against the corrosive action of fluorine.

The surface of equipment operating with fluorine must have an excellent mechanical finish which excludes the presence of pores, cracks, etc. Welded seams must be checked by x-rays for the absence of cracks or any inclusions. Any kind of flaws of the metal surface

or the welded seam may become the cause for its ignition on contact with fluorine.

Ignition of equipment material may also be brought about by a high-speed fluorine flow which, obviously, washes away the protective fluoride film at some spots of the metal surface which then become ignition centers. If for some reason a metal is ignited in a fluorine atmosphere, it will violently burn until all of the fluorine is exhausted or all of the metal burns out.

Like liquid oxygen, liquid fluorine continuously boils liberating extremely poisonous vapors which, at the same time, are highly inflammable.

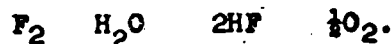
Storage, transport and filling of liquid fluorine are incomparably more complex than those of liquid oxygen. Small spillings of small liquid fluorine are usually neutralized by sodium bicarbonate which not only neutralizes fluorine but helps extinguishing the fire breaking out as a result of the ignition of organic substances on contact with liquid fluorine. Reacting with the latter, sodium bicarbonate releases carbon dioxide which, as is known, is a fire extinguisher.

In the USA liquid fluorine is stored and transported in a supercooled state, i.e., at a temperature below its boiling point. For this reason containers of several tons' capacity are made up of three tanks placed one within the other. Liquid fluorine is filled in the innermost tank, and the coolant (usually liquid nitrogen) in the second one. For insulation, air is removed from the space between the second and the third tank whereupon it is filled with heat-insulating material. The innermost container filled with liquid fluorine is hermetically sealed. Because of

the difference in the boiling point of liquid nitrogen and liquid fluorine (about 13 to 14°), the latter does not boil in such containers and, hence, it does not liberate toxic and inflammable vapors. Containers so designed are suitable for storing liquid fluorine in warehouses or for its transport by truck or rail. To prevent spilling in the case of accidental destruction of feedlines, all of the pipe outlets in reservoirs are made through the top of the tank. Unloading from the tank is effected by gas (helium or nitrogen) pressurization.

The following data give us an idea of the toxicity of fluorine. Concentrations of 25 to 50 parts per 1 million parts per volume of air are fatal to man after 15 minutes. Concentrations of 15 to 25 parts per 1 million parts per volume of air cause heavy injuries to the lungs, and only concentrations of 10 or less parts per 1 million parts of air per volume do not represent a hazard to man after 15 minutes.

The vapors freed during the boiling of fluorine can be neutralized by mixing them with vapors (steam). Fluorine reacts with water vapors according to the formula



As a result, hydrogen fluoride and oxygen are formed. The former is a lesser hazard to the organism than elemental fluorine, its toxicity being about 1/10 of the latter. Moreover, it is well miscible with water, hence it can easily be transferred in aqueous solutions with their subsequent neutralization (detoxication). This is conveniently done with calcium oxide which transforms hydrogen fluoride in harmless calcium fluoride



When testing rocket propellants operating with fluorine,

combustion products of hydrogen in fluorine can be neutralized also by this method.

Small amounts of liquid fluorine can be eliminated by burning carbon in them. To do this fluorine is pumped through drums containing coal. On contact with the coal there occurs a reaction forming a non-toxic gaseous substance, carbon tetrafluoride, which can be safely released in the air:



As a rocket propellant oxidizer, fluorine, because of its exceptionally powerful reactivity with all the known fuels, forms hypergolic propellants. Consequently, reactive engines operating with liquid fluorine have no need for special igniting devices and are therefore much simpler in design.

Propellants based on elemental fluorine have also higher combustion rates because of the high reactivity of this element. For the total combustion of a fuel with fluorine a shorter stay time in the engine chamber is required than for any other propellant. This makes it possible to build engines with smaller combustion chambers than those operating with oxygen and nitric-acid propellants.

Fluorine-base propellants are only then more powerful than those based on oxygen if substances with a high hydrogen content are used as fuel. With hydrocarbon fuels, fluorine oxidizers form ineffective propellants.

For this reason liquid fluorine, like other fluorine oxidizers, is expediently applied with such fuels as ammonia, hydrazine, and liquid oxygen.

The propellants formed by fluorine oxidizers with hydrazine

derivatives (methyl hydrazine, dimethyl hydrazine and others) are less effective since the molecules of these derivatives contain carbon atoms. It is pointed

It is pointed out that on the basis of fluorine oxidizers highly effective rocket propellants can be formed if metals, metal-organic compounds or metal particles suspended in liquid fuels, e.g., hydrazine or methyl hydrazine (metal suspensions) are used as fuels.

Unlike oxides, metal fluorides have, as a rule, a lower boiling point, hence they will be in a gaseous state in the combustion chamber and the nozzle. Moreover, the same fuels burning in fluorine and in oxygen develop higher temperatures in fluorine, and this also contributes to the formation of gaseous combustion products of metals and other highly caloric substances.

Some substances, such as silicon, form with fluorine compounds (under the release of large amounts of heat) which are gases even under normal conditions. Burning of silicon in oxygen forms silicon dioxide SiO_2 with a very high boiling point (1900°C). Table 4 gives the boiling points of oxides and fluorides of some fuels which can be used as rocket propellant components.

Table 3

Boiling Point of some Metal Oxides and Fluorides

Fuel	Oxide formula	Oxide boiling point $^\circ\text{C}$	Fluoride formula	Fluoride boiling point $^\circ\text{C}$
Beryllium	BeO	3900	BeF_2	850
Aluminum	Al_2O_3	2700	AlF_3	1110
Magnesium	MgO	2250	MgF_2	1110

Chlorine trifluoride

Of all the fluorine compounds this is the most interesting one as a rocket propellant oxidizer. Compared with elemental fluorine, it is less powerful since its molecule comprises a chlorine atom which is a very bad oxidizer and propellants based on it are completely ineffective. However, chlorine trifluoride has a comparatively high boiling point (13.8°C) and a low temperature of solidification (-111°C) which greatly facilitates operations as compared with other fluorine-base oxidizers. At ambient temperature it can be stored in hermetically sealed containers at pressures up to 2 to 3 kg/cm^2 .

In reactivity, chlorine trifluoride is second only to fluorine. In fact, it reacts with most substances. Even water oxidizes on contact with it. The combustion process of water in chlorine trifluoride is very violent and is accompanied by a conspicuous release of heat and a visible flame. In spite of its high reactivity, its storage and transport turned out to be less complex as regards its corrosive action on containers and equipment, than that of such widely used rocket propellant oxidizers as nitric acid and its mixtures with nitric acids.

Chlorine trifluoride can be stored for long periods in containers made of common carbon steel. A fully satisfactory corrosion resistance to the oxidizer is also exhibited by such metals as copper, brass, magnesium and others. Stainless steel, nickel and Monel metal are also fairly resistant. As packing material in apparatus operating with chlorine trifluoride, copper and teflon saturated to a strength of 40% with copper fluoride can be used.

This apparatus must not be made of glass, asbestos or materials

containing silicon since chlorine trifluoride, like other fluorine oxides, reacts with the substances to form gaseous silicon fluoride.

Chlorine trifluoride is as toxic as fluorine. It can only be handled in special gas masks and protective clothes. The hazard in operating with it arises not only from breathing its vapors but also from drops hitting clothes, fabric, the skin or rubber which are immediately ignited by it. Hence its handling requires exceptional safety measures.

Elimination of large amounts of it poses a serious problem since there are very few substances which can dissolve it without reacting. It is well soluble in carbon tetrachloride and some nitric compounds and does not react with them in the cold. At certain ratios, however, chlorine trifluorine mixtures with these substances may explode from comparatively external stimulation (impact, flame and others).

The properties of chlorine trifluoride show, as a whole, that it has certain advantages over liquid fluorine as regards operation but its handling is, none the less, quite complex and dangerous.

A feature of this substance is its high density (1.78 g/cm^3) compared with that of other oxidizers. The chemical reactivity of chlorine trifluoride which creates difficulties in handling it, is actually an advantage when it is used in engines. But with all the known fuels it forms hypergolic propellants with a high burning rate in the combustion chamber.

Fluorine Monoxide

Its molecule consists of atoms of the two most powerful oxidizers, fluorine and oxygen. Under normal conditions it is a gas as toxic as pure fluorine.

Its boiling point is -145°C . This chemically stable substance can be stored for long periods of time without noticeable decomposition in containers made of stainless steel, nickel, or Monel metal. Density of liquid fluorine monoxide at boiling point is 1.52 kg/litre, i.e., it is almost equal to that of liquid elemental fluorine.

Organic and anorganic combustibles ignite on contact with it. Handling of fluorine monoxide as complex and dangerous as that of liquid fluorine. Its storage, like that of liquid fluorine, requires complex devices by which to maintain low temperatures and prevent its vapors from penetrating in the surrounding air.

Fluorine monoxide has all the operational disadvantages of liquid fluorine, and, in addition, it is noticeably less powerful. In fact, it rates between liquid oxygen and liquid fluorine in terms of power and efficiency. The thermodynamic computation of propellants based on liquid fluorine, oxygen and fluorine monoxide with hydrazine at a pressure of 21 kg/cm^2 within the combustion chamber and 0.84 kg/cm^2 at nozzle exit plane for an engine operating in the vacuum yields the following specific impulses:

Liquid fluorine	hydrazine.....	417 kg sec/kg
Liquid fluorine monoxide	hydrazine	390 kg sec/kg
Liquid oxygen	hydrazine	360 kg sec/kg

Thus, fluorine monoxide which is appreciably inferior to elemental fluorine in terms of power and has virtually no advantages as regards handling and operating with it, obviously cannot be regarded as an especially successful rocket propellant oxidizer of the future.

Tetranitromethane

Under normal conditions tetranitromethane, $C(NO_2)_4$ is a yellow-green liquid which freezes at $13.8^\circ C$. Unlike water, it reduces its volume at freezing, hence there is no danger that the liquid may destroy hermetically sealed containers if it freezes in them.

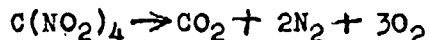
If heated to about 100 to $120^\circ C$, it begins to decompose and releases nitric oxides. At $126^\circ C$ it boils and decomposes at the same time.

A feature of tetranitromethane as a rocket propellant oxidizer is its great density. Moreover, like nitric acid and the oxidizers based on it, it has a high boiling point.

Compared with nitric acid, it has a very low corrosive action with respect to most materials. It may be stored and transported in containers of common carbon steel. Only copper and its alloys are attacked by this oxidizer.

Pure tetranitromethane is a chemically stable substance but alkali impurities initiate its decomposition with the formation of explosive nitroform salts. As a rocket propellant oxidizer, tetranitromethane has two substantial disadvantages responsible for the fact that this extremely powerful oxidizer has up to now not been practically employed in rocket technology: first, it has a high temperature of solidification; secondly, under specific conditions it has a tendency to explosive decomposition.

Its explosiveness is due to its being formed with heat absorption, i.e., it is an endothermic compound. Hence its decomposition, accompanied by liberation of heat, takes place according to the following equation:



The heat released amounts to about 450 kcal/kg .

It should be noted that explosiveness of pure tetranitromethane is low under normal operating conditions of rocket propellants. Only a very powerful stimulation can initiate its explosive decomposition. Addition of combustible impurities, however, make it extremely sensitive to outside stimulation. ^{With a} content of 1 to 1.5% of such hydrocarbons as kerosene, it readily explodes from the action of a standard detonator fuse or even from weaker stimulation.

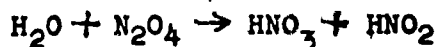
The explosive of tetranitromethane is very destructive. Most sensitive and destructive are mixtures with hydrocarbon fuels containing close to 15% of the latter. Concentrations of greater strength again reduce the explosiveness of tetranitromethane, and with more than 60% hydrocarbon fuels it can no longer be exploded by a standard denonater fuse. Hence when handling tetranitromethane it must be carefully kept free of impurities, especially those of organic origin.

The explosiveness of tetranitromethane can be reduced by adding to it nonorganic substances. Already before World War II, mixtures with 30% liquid nitric oxides were tested in Germany. Such mixtures are extremely powerful as rocket propellant oxidizers and have a low sensitivity to external stimulation. They do explode nevertheless, if stimulation is sufficiently powerful. A disadvantage of tetranitromethane is its high freezing point.

Oxidizers based on tetranitromethane with a low freezing point (of the order of -40 to -50°C) are difficult to develop due to the fact that in it are well soluble nearly all the hydrocarbon fuels while nonorganic substances are almost insoluble. To lower its freezing point by adding combustibles to it is impossible because highly sensitive mixtures are so formed.

Studies were undertaken in the USA on the subject of lowering the freezing point tetranitromethane. The best results were obtained with liquid nitrogen tetroxide. These mixtures are not only relatively insensitive to external stimulation but they also have a lower freezing point than pure tetranitromethane. Thus, a mixture of 35% nitrogen tetroxide and 65% tetranitromethane has a freezing point near -30°C . A drawback of these mixtures is their high vapor tension and high volatility. For this reason they can only be stored in hermetically sealed containers.

One of the advantages of tetranitromethane is its low corrosive action. Mixtures with nitric oxides are likely to be more aggressive against construction materials. Although anhydrous nitric oxides are, like tetranitromethane, non-corrosive substances, even a slight moisture content enhances their corrosiveness by the appearance of nitric acid. The latter forms in accordance with the following formula:



Mixtures of tetranitromethane and nitrogen tetroxide are more volatile than pure tetranitromethane. The first to evaporate are nitric oxides which, if the oxidizer is stored in a non-hermetic container, reduce the nitrogen tetroxide content and, hence, change the oxidizer's freezing point. To lower its freezing point, mixtures with methyl nitrate and nitromethane were tested. These mixtures are less effective than that with nitrogen tetroxide since their freezing point is higher and they are dangerous in handling.

Additives lowering the freezing point of tetranitromethane not only impair some of its operating properties but also reduce its power. Rockets operating with a fuel based on a tetranitromethane oxidizer containing any one of the additives above, have a shorter

range than rockets powered by a propellant based on pure tetranitromethane, oxidizer.

Chapter III

FUELS

Combustion is a turbulent exothermic chemical reaction in the presence of a flame. Most frequently this reaction occurs when atoms of various elements combine with oxygen or fluorine atoms.

Table 4

Calorific Value of Combustibles			
Combustible	Density, kg/l	Calorific Value of Combustibles, kcal/kg	
		In oxygen	In fluorine
Hydrogen	0.07	28 700	64 000
Beryllium	1.85	16 150	
Boron	2.30	13 900	
Lithium	0.53	10 230	20 800
Carbon	2.25	7 800	13 780
Aluminum	2.70	7 400	12 190
Silicon	2.40	7 370	12 190
Magnesium	1.74	5 920	
Titanium	4.50	4 530	

The effectiveness of a fuel is determined in the first place by its calorific value and its gas-generating capacity. Table 4 gives the calorific value of some combustible elements burning in oxygen or fluorine.

We can see from the Table that hydrogen has the highest heating value. It also evolves a large amount of gas during combustion. However, considerable difficulties arise in the application of pure liquid hydrogen as a rocket propellant

component. On the other hand, its mixtures with some elements have physico-chemical properties fully suitable for this purpose, but are less powerful.

Second in calorific value after hydrogen is beryllium. Yet, neither pure nor in compounds with other substances, this element can be of any practical value as a rocket propellant for the following two reasons: it is highly toxic (this applies also to its compounds); secondly, it is very rare and, hence, extremely expensive.

Boron is slightly less powerful than beryllium but it is fairly common, hence it may be of practical use as a fuel component of rocket propellants.

Carbon has an even lower heating value and a relatively low gas generating capacity. Nevertheless, it is present in a large group of chemical combinations known as organic compounds.

Section 10. Fuels of Organic Origin

To this class belong, in the first place, the various fuels obtained from the distillation of petroleum and known as petroleum products. Widely used in rocket technology are kerosenes.

Essentially, these fuels are a mixture of chemical compounds consisting of a highly effective combustible element, hydrogen, and a less effective one, carbon. Fuels of this class are known as hydrocarbons. The chemical combination of the two elements above yields substances less powerful than elemental hydrogen but considerably more powerful than elemental carbon. Their physico-chemical properties defining the expediency of their utilization

are incomparably higher than those of carbon and hydrogen.

All of the petroleum products used as rocket propellant components are liquids with high boiling points and low temperatures of solidification, having a fairly high stability against decomposition from heating. A drawback of these fuels is the instability of their chemical composition, hence such indices of a fuel of the same brand as density, viscosity, surface tension and others vary from supply to supply. This, however, is inadmissible for rocket propellant components since the indices above do substantially affect the performance of the engine.

The instability of physico-chemical properties of petroleum products can be explained by the fact that these fuels have an inhomogeneous chemical composition and are mixtures of a large number of hydrocarbons evaporating by boiling in a given temperature range. In producing one and the same fuel brand from petroleum of various oil fields, constancy of temperatures at the beginning and the end of the boiling process can be easily maintained whereas, as a rule, the content of the various chemical compounds in the fuel is not constant.

Only those fuels which are homogeneous chemical substances and whose composition can easily be checked, can have stable properties. Investigations are being conducted in the USA for the synthetic production of hydrocarbons which by their power and operational properties could replace petroleum-type fuels and at the same time have stable physico-chemical properties not changing from supply to supply. It is planned to use these fuels with newly designed rockets as well as with existing ones operating with petroleum-type fuels. Thus, for example, a synthetic hydrocarbon

fuel is being developed for the "Atlas" rocket powered by a propellant whose fuel component is the RP-1 aircraft fuel. The new, synthetic fuel will be a compound with the same physico-chemical properties as the RP-1. Three hydrocarbons have been found which can replace the latter.

Investigations into new hydrocarbon fuels are also conducted in other directions. As already noted, rocket fuel density is an important characteristic. As a rule, oxidizers have a density 1.5 to 2.0 times that of fuels, this being a disadvantage common to all fuels. Increased density makes it possible to reduce the size of the rocket by reducing the size of the fuel tank and maintaining the same useful load and the same range.

High-density hydrocarbon fuels are chiefly extracted from coal tar. Some of them have, besides high density (up to 1.5 kg/liter), also high efficiency indices. Thus, e.g., decahydronaphthalene has a calorific value greater than kerosene extracted from petroleum. In spite of their high density, these fuels have not been practically exploited in rocket technology as yet because of a number of disadvantages inherent in them, such as high viscosity, high temperature of solidification, and others.

Alcohols, especially ethyl and methyl alcohol, are the next class of fuels. They played an important role as propellant components in the early days of rocket technology.

Alcohol molecules consist of oxygen, carbon and hydrogen atoms. Since the combustible carbon and hydrogen atoms comprised in alcohols are already partly oxidized, the heating value of propellants whose fuels are alcohols, is considerably lower than that of propellants with hydrocarbon fuels. This we can see from Table 5

which gives the calorific value of alcohols compared with that of a hydrocarbon (kerosene).

Table 5

Calorific Value of Oxygen-Carrying Propellants
Excess oxidant ratio $\alpha = 1$

Fuel	Fuel density, kg/l	Propellant density kg/l	Calorific value kcal/kg
Methyl alcohol	0,796	1.0	1870
Ethyl alcohol	0.8	1.03	2085
Kerosene	0.82	1.07	2400

Density of alcohols is virtually the same as that of hydrocarbons. The density of alcohol-base propellants, however, is lower than that of propellants based on kerosene. This is due to the fact that the combustion of a unit of weight of alcohol requires a lesser amount of oxidizer than the same amount of kerosene. But since the density of any oxidizer is higher than that of the fuels mentioned, the propellant with a higher oxidizer content has a higher density.

In the early days of rocket technology, when the great amount of heat liberated per unit volume of combustion space created unsurmountable difficulties in ensuring a reliable cooling for rocket engines, the calorific value of propellants with alcohol fuels was sufficient. Moreover, to reduce propellant combustion temperature and at the same time improve the cooling properties of the fuel, water was added to them. At the present time there still exist rockets powered by alcohol propellants (for

example, the American rocket "Redstone" with a 480-km range) but the new rockets are designed for other fuels. At the present stage of rocket technology the problem of cooling rocket engines operating with highly calorific propellants is fully solvable. Apparently alcohols as the fuel of rocket propellants have already become obsolescent.

Amines are the next class of fuels. They are obtained by replacing in an ammonia molecule NH_3 two or even three hydrogen atoms by hydrocarbon radicals. Depending upon the amount of hydrogen atoms replaced, amines may be primary (only one hydrogen atom is replaced by a radical in ammonia), secondary (two atoms are replaced) and tertiary (all three atoms are replaced).

There exists a large variety of amines, but to rocket technology only those are interesting which under normal conditions are liquids with high power factors and acceptable operational properties.

A characteristic of amines distinguishing them from petroleum products and alcohols is their increased reactivity which changes depending on the replacement in the ammonia molecule of hydrogen atoms by hydrocarbon radicals, and of the radicals themselves.

Amines react with nitric-acid oxidizers to form hypergolic propellants.

A disadvantage of amines is their considerably higher cost than that of petroleum products and their high toxicity which affects both the unprotected parts of the body and the respiratory system. Such an aromatic amine as aniline has a toxicity 200 times that of kerosene (i.e., the permissible concentration of kerosene vapors in the air is 200 times greater than that of

anilin vapors) and twice that of such highly toxic a substance as nitric acid. The hazard in handling amines is aggravated by the fact that unlike nitric acid they have no characteristic odor, hence a man may operate for some time in an atmosphere polluted with amine vapors, be seriously poisoned and suffer the consequences only after some time. Amines hitting unprotected parts of the body do not strongly irritate them but have the property of penetrating through the skin into the organism where they produce harmful effects.

Section 11. Hydrazine Fuels

The simplest representative of this class of fuels (hydrazine) has the formula $\text{H}_2\text{N}-\text{NH}_2$. Characteristic for this substance is the fact that its molecule contains only one type of combustible atom, hydrogen, while nitrogen during combustion only increases gas generation and evolves in combustion products in a free form.

Since the combustible part of hydrazine is made up of 100% hydrazine, it has a high calorific value.

Hydrazine molecules are formed from nitrogen and hydrogen atoms under absorption of heat, hence it is an endothermic substance, this being the second cause for the substance's high calorific value.

Its advantages as a rocket fuel are also its high density (1.04 kg/liter) and high boiling point (113°C).

Hydrazine, however, has considerable shortcomings. Under normal conditions it is a transparent liquid freezing at $+1^\circ\text{C}$. Such a high freezing point makes it inconvenient to operate with hydrazine especially in the winter. If stored or filled into the rocket during the cold season, it must be warmed. An even greater drawback is its tendency to explosive decomposition under heating or from impacts. There are also other disadvantages of lesser

importance: oxidation: from the reaction with air oxygen, its hygroscopic nature, and others, which somewhat complicate its handling but are fully surmountable.

Hydrogen atoms in the hydrazine molecule can be replaced by other atoms or atom groups. Compounds in which hydrogen atoms are replaced by hydrocarbon radicals (methyl CH_3 , ethyl C_2H_5 and others) are known as alkylates of hydrazine. A number of them was obtained, and they differ from hydrazine proper by their physico-chemical properties (density, viscosity, etc.) and calorific value.

Among these, the most interesting ones as rocket fuels are methylhydrazine $\text{CH}_3\text{HN-NH}_2$ and unsymmetric dimethylhydrazine $(\text{CH}_3)_2\text{N-NH}_2$. These substances are less powerful than hydrazine since their molecules, beside hydrogen, contain a considerable amount of carbon which has an appreciably lower calorific value. Their advantage consists in the fact that they are liquid over a wide range of temperatures which considerably facilitates their utilization.

Best known abroad are at the present time the properties of unsymmetric dimethylhydrazine. It is a liquid freezing at -57.2°C , boiling at 63.1°C , with a density of 0.783 kg/liter at 20°C .

Characteristic of dimethylhydrazine is its high reactivity. Even more than hydrazine, it combines with oxygen from the air yielding dimethylamine and water. It reacts with carbon dioxide from the air to form $(\text{CH}_3)_2\text{N-NH}_2\frac{1}{2}\text{CO}_2$ salts which are not soluble in dimethylhydrazine and therefore form a solid deposit. When stored, dimethylhydrazine must not come in contact with the air because of its high reactivity. It is best stored under a slight

pressure from a neutral gas, e.g., nitrogen.

Pure dimethylhydrazine does not attack construction materials. Some water in it promotes corrosion of aluminum and its alloys.

It has a fairly high heat resistance and begins to decompose only at about 700 to 800°C. Unlike hydrazine, neither liquid nor gaseous dimethylhydrazine explodes from impacts but easily ignites in air (ignition temperature 1°C, self ignition at 250°C), hence it must be regarded as inflammable.

Dimethylhydrazine should be stored in special containers far away from other buildings. The containers should be placed underground since the smallest spark from static electricity may cause a fire.

It can be extinguished with water, being miscible with it at all ratios. Water dilutes dimethylhydrazine and cools it at the same time. Diluted with two or three parts water, it no longer burns in the open air. Another effective extinguisher is carbon dioxide, whereas chemical foams commonly used as fire extinguishers, are unsuitable for this purpose.

The high chemical reactivity of dimethylhydrazine makes it a valuable propellant component. With liquid oxygen it yields a propellant with forced ignition, and with nitric-acid oxidizers it forms hypergolic propellants. Compared with other self-igniting components, dimethylhydrazine has a very short ignition delay with nitric-acid oxidizers (of the order of 0.005 sec) which depends but slightly on the temperature of components.

It is well soluble not only in water but also in hydrocarbon fuels. It is therefore possible to obtain hypergolic fuels based on dimethylhydrazine with the aid of commonly available and inexpensive petroleum products such as kerosene. Self-igniting

fuels with an acceptable ignition delay time (not exceeding 0.03 sec) are obtainable by mixing it with kerosene. The content of the latter may attain 40%. Dimethylhydrazine-kerosene mixtures change their ignition delay time on contact with nitric-acid oxidizers more abruptly with increasing temperatures than pure dimethyl hydrazine.

Being a highly toxic substance, it must be handled with the greatest care. All hydrazine fuels have the same properties as alkalis, but unlike the latter they cause no irritation of the skin. Nonetheless there must be kept away from it because they penetrate into the body where they are very harmful. Dimethyl - hydrazine has a sharp characteristic odor. Very small amounts of it can be detected in the air. Toxicity of hydrazine and dimethyl-hydrazine is twice that of nitric acid. Protective goggles and gloves are recommended for the handling of smaller amounts, whereas larger amounts require protective suits. As soon as dimethyl-hydrazine odor is detected in the air, gas masks must be put on. Splashes of the substance can be washed from the clothes with large amounts of water. Prior to reusing the clothes, they must be thoroughly washed. Dimethylhydrazine is a powerful poison, hence it may not be poured into the drain system under any circumstance.

Section 12. Fuels of the Future

It was said earlier that of all chemical fuels hydrogen has the highest calorific value. The high efficiency of rocket propellants based on hydrogen is due on the one hand to its high calorific value and, on the other, to the low molecular weight of combustion products formed. It was held until recently that

under service conditions liquid hydrogen would be so inconvenient and hazardous to handle that it might never be used as a component of rocket propellants.

The main drawback of liquid hydrogen is its low boiling point which is -254°C , i.e., 71°C below that of liquid oxygen. This causes difficulties in storing and transporting large amounts of liquid hydrogen.

Low density (0.07 kg/liter) is another serious disadvantage.

Mixtures of hydrogen with air over a wide range of ratios are highly explosive and this is a third disadvantage creating conspicuous difficulties. Mixtures containing from 4 to 74% hydrogen explode from the smallest shock, impact, spark.

Hazards in handling liquid hydrogen may arise from contaminations with oxidizers or from accidental spillings and leaks. To prevent explosions, pipes and containers must periodically be blown through with an inert gas. In the case of leaks, the premises must be rapidly cleared of hydrogen vapors by means of thorough ventilation. To reduce the hazard from explosive air-hydrogen mixtures, all equipment operating with liquid or gaseous hydrogen should be placed out of doors where hydrogen vapors can diffuse in the air without creating dangerous concentrations. To prevent air oxygen from penetrating into the equipment and containers filled with liquid or gaseous hydrogen, these must always be kept under a small excess pressure.

Practice shows that hydrogen spillings present no serious hazard if there is no ignition source nearby. Small spillings evaporate very rapidly and hydrogen diffuses in the atmosphere. When ignited, it burns smoothly, without explosional. Its flame is colorless, hence it is invisible in daylight.

Storing liquid hydrogen, as any other low-boiling liquid, entails evaporation losses, the prevention of which is complicated by its extremely low boiling point.

Among the features of liquid hydrogen as a rocket propellant component, its high energy and good cooling power should be noted. Compared with hydrazines and petroleum products, hydrogen forms propellants with appreciably high specific impulses. Yet, they have a very low density. Hence it is obvious that liquid hydrogen can only be effective if used in super-long range rockets for which propellant density is far less important than specific impulse.

At the present time, the problems relating to storage, transport, transfer as well as production of liquid hydrogen are basically solved. The USA are intensively working on the design of rocket engines powered by liquid hydrogen and oxygen. Pratt-Whitney has developed a reactive engine with a 7-ton thrust which uses liquid hydrogen as a fuel and liquid oxygen as the oxidizer.

The creation of an operating rocket engine powered by liquid hydrogen shows that the difficulties in operating with this fuel are by no means unsurmountable. Considering its high energy as well as the availability and low cost of the raw material for its production (hydrocarbons derived from petroleum distillation), it may be expected that it will be widely used in rocket technology in the near future.

Boron Hydrides

Their molecule comprises atoms of two elements with the highest calorific value, boron and hydrogen. Boron, like carbon, forms a large number of compounds with hydrogen which has various physico-

chemical properties.

The energy factors of boron hydrides depend on their elementary composition. The higher the number of hydrogen atoms per boron hydride fuel, the greater is its calorific value and its gas-forming capacity.

The simplest representative of this class of compounds is diborane, B_2H_6 , under normal conditions a gas igniting on contact with air. Compounds with a higher molecular weight are under normal conditions either liquid or solid. Thus, pentaborane, B_5H_9 , is a liquid boiling at $58^\circ C$ and solidifying at $-47^\circ C$. Its density at $20^\circ C$ is 0.72 kg/liter. Decaborane, $B_{10}H_{14}$, is a white crystalline solid.

The most interesting one as a jet fuel is pentaborane. Its density is about 10% less than that of gasoline but its calorific value exceeds that of gasoline by 54%. It may be a valuable fuel for turbo-jet and ram-jet engines. A characteristic feature of pentaborane is its high rate of combustion in the engine chamber, exceeding by several times that of conventional hydrocarbon fuels. This property permits the design of engines with short combustion chambers. Consequently, the size of the aircraft itself may also be considerably reduced.

Gaseous and liquid boron hydrides are thermally unstable compounds. On heating they decompose so intensively that decomposition occasionally ends in an explosion. This property complicates operations with these compounds. This is further complicated by their exceedingly high toxicity. In fact, diborane and pentaborane vapors are four to five times more poisonous than nitric acid vapors.

A disadvantage of boron hydrides is their low density. Some

of them have a low self-ignition point. Thus, pentaborane ignites spontaneously at $+65.5^{\circ}\text{C}$. If stored under natural conditions, such a fuel may spontaneously ignite in the summer.

By replacing in the boron hydride molecule one or several hydrogen atoms by a hydrocarbon radical we can obtain the so-called boron hydride alkylates which have better operational characteristics than the boron hydrides themselves. Alkyl boron hydride molecules consist of atoms of three elements, boron, hydrogen and carbon. The presence of carbon atoms somewhat lowers their calorific value with respect to that of boron hydrides, but at the same time it increases its density, considerably reduces toxicity and increases heat resistance.

In the USA, jet engines are powered by alkyl boranes of two brands, HEF-2 and HEF-3. By the physico-chemical properties of these fuels it may be assumed that HEF-2 is ethyl pentaborane, $\text{C}_2\text{H}_5\text{B}_5\text{H}_8$ and HEF-3 is ethyldecaborane, $\text{C}_2\text{H}_5\text{B}_{10}\text{H}_{13}$. Under normal conditions these borohydrocarbons are liquids. Their density is of the order of 0.8 to 0.83 kg/liter while that of pentaborane is only about 0.62 kg/liter. Their burning rate in the engine combustion chamber is considerably higher than that of conventional hydrocarbon rocket fuels.

Introduction of a carbon atom in the boron hydride molecule sharply reduces its toxicity. Thus, if pentaborane is 400 to 600 times more toxic than aviation gasoline, ethylpentaborane is virtually as poisonous as are petroleum products. Borohydrocarbon fuels have a higher stability than boron hydrides. They do not decompose under the effect of moisture or if heated to a temperature not exceeding 250°C . Yet, they have a considerably

lower thermal stability than hydrocarbon compounds. If stored for long periods of time at ambient temperature they are subject to polymerization⁴ which yields solid, unsoluble substances which are being readily deposited. The presence of impurities in borohydrocarbon compounds enhances polymerization.

Table 6 gives the calorific values of diborane, some borohydrocarbon compounds and kerosene as they burn in oxygen.

Table 6

Calorific Value of Boron-Hydrocarbon Compounds and Kerosene

Compound	Formula	Calorific value of fuel kcal/kg
Diborane	B_2H_6	17 390
Methyl diborane	$CH_3(B_2H_5)$	14 400
Tetraethyl diborane	$(C_2H_5)_2B_2H_2$	11 700
Ethyl diborane	$C_2H_5(B_2H_5)$	13 900
Triethyl borane	$B(C_2H_5)_3$	11 100
Kerosene	$C_{7H_{16}}$	10 230

We see that the calorific value of all the borohydrocarbon compounds is higher than that of kerosene but lower than that of the starting mixture, boron hydride-diborane.

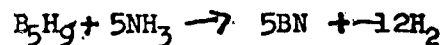
Boron-containing fuels have a high heating value, but they are used only with ram-jet and turbo-jet engines powered by conventional fuels, the boron-containing fuel being injected behind the turbine. These fuels cannot be used with turbo-jet engines as

the basic fuel since the combustion products of boron, boron oxide, has a high boiling point (1500°C). Hence in the engine combustion chamber, along with gases, solid boron oxide particles will be formed which during passage of propellant combustion products through the turbine form an incrustation on the impeller blades which disrupts the turbine's normal operation.

The expediency of using boron fuels with rocket engines powered by liquid compellants appears to be doubtful. The chief disadvantage of these fuels can in this case be explained by the high molecular weight of the combustion products of boron (e.g., B_2O_3 has the molecular weight 60), hence the efficiency of propellants with boron-containing fuel components exceeds only slightly that of propellants with conventional hydrocarbon fuels.

High energy propellants based on boron hydrides can be obtained if nitrogen-containing substances are used as oxidizers. In such combinations the role of oxidizer is played by the nitrogen atom. There is reason to believe that when nitrogen combines with boron, large amounts of heat are evolved since boron nitride, BN, appears to be a substance having a great heat of formation.

Reaction between boron hydride and nitrogen hydride (ammonia or hydrazine) takes place according to the following equation:



This yields a solid, boron nitride, and releases large amounts of elemental hydrogen. Hence the mean molecular weight of the flue gases of such a propellant will be close to that of hydrogen, viz., 2. Preliminary computations show that despite a high percentage by weight of solid boron nitride particles, in combustion products of the propellant boron hydride plus nitrogen

hydride it will highly efficient if used in rocket engines.

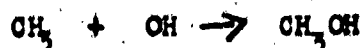
Boron, as well as some metals (aluminum, magnesium), combustion of which evolves large amounts of heat, can be used with fuel components of rocket propellants as additives in the form of fine powders (suspensions) to liquid hydrocarbons. The possibility of preparing a suspension of metal powders in kerosene with a solid phase content up to 50% has been experimentally proved. Such compounds have a good fluidity which permits them to be normally fed into the combustion chamber of the engine. Combustible suspensions warrant specific impulses in ram-jet aircraft engines exceeding by 50% those resulting from pure kerosene. Combustion of the latter requires appreciably more oxygen than combustion of the same amount of metals (3- to 3.5-fold). Combustible suspensions are therefore particularly valuable for high-altitude flights. The ceiling of aircrafts powered by such fuels will be higher than if they were powered by conventional aviation gasoline.

At the present time, aluminum, boron and magnesium are technically accessible substances considered suitable for preparing metal-base fuels. Magnesium is highly reactive, hence it has also a higher burning rate in the engine chamber. It is easier ground into fine powder than other metals, this being one of the primary conditions for preparing suspensions with acceptable properties (fluidity, stability, completeness of combustion in the engine). For this reason magnesium suspensions in hydrocarbon fuels are of the greatest interest. It should be borne in mind that metal-base fuels yield good results only if used with ram-jet engines. Because of the high boiling point

of metal oxides and the considerable molecular weight of combustion products their use in rocket engines is not likely to be expedient.

Free Radicals

This is one of the possible energy sources for rocket technology. Free radicals are fragments of molecules having no charge. Molecules can be disintegrated by the action of various factors, e.g., heat, irradiation, etc. Thus, if a methyl alcohol molecule, CH_3OH , is heated to high temperatures it will break up into radicals, the methyl radical CH_3 , and the hydroxyl radical OH . Such a cleavage requires large amounts of heat. When the methyl and hydroxyl radicals recombine there again forms a molecule



of methyl alcohol, and the amount of heat evolved is equal to that used for the dissociation of that molecule.

Free radicals are obtainable not only from molecules of complex substances but also from those of such simple substances as hydrogen, oxygen, nitrogen and others. Dissociation of molecules of simple substances yields radicals in the form of free atoms.

The state of a substance in the form of free radicals is highly unstable. At ambient temperature and pressure, free radicals can practically not exist, they combine with each other to form stable molecules and evolve heat. The merit of free radicals as a source of energy is their high calorific value. Conversion of one kilogram atomic hydrogen to molecular hydrogen

evolves an amount of heat equalling 50,000 kilocalories. Molecular hydrogen may during this process attain a temperature of 12,000°C. Recombining of free atoms of other simple substances or fragments of molecules of complex substances involves the liberation of lesser amounts of thermal energy than when hydrogen atoms combine. However, free radicals even if obtained from the dissociation of heavy molecules of complex substances have a heating value 5 to 10 times that of common bipropellants.

As an energy source, the application of free radicals is at an initial stage. No practically applicable methods for their large-scale production, lasting storage or measures ensuring safety in handling them have been devised as yet. At the present time investigations into the nature of free radicals are being conducted in laboratories abroad. These studies are being carried out at very low temperatures in a high vacuum, since only under these conditions a more or less lasting existence of free radicals can be ensured.

Their durable storage represents one of the toughest problems. Some samples obtained in the laboratory could be stored, before they combined, for varying periods of time depending on storage conditions. Thus, neon atoms from the moment they were obtained in an unsteady state until they convert to a stable condition can be stored at -263°C during 25 sec. At -268°C they can be kept for years.

As a source of energy free radicals are interesting not only in their pure form but also as mixtures with conventional rocket propellant components. If, e.g., liquid oxygen contains only about 1% free radicals (atomic oxygen), the energy factors of propellants based on such an oxidizer (together with a fuel)

will exceed by 20% those of common oxygen propellants with the identical fuel.

* * *

At the present time the development of rocket technology has reached very high levels, especially in the Soviet Union, the country of the builders of Communism. Manned space-ships capable of staying in orbit for long periods of time are evidence of the fact that the day when man will set foot on other planets of the solar system and return to the earth is no longer far away.

The designs of space ships and their control systems have reached a high degree of sophistication, as is evidenced by the successful flights of Soviet cosmonauts. Yet, great difficulties are still in the way of manned flights to other planets of the solar system. These difficulties are chiefly due to an insufficient efficiency of propellants used at the present time by rocket technology. Computations show that a space-ship capable of taking a man to the moon and returning him to the earth is bound to have a considerable weight, most of it made up by the propellant.

Liquid rocket propellants in use today have a comparatively concentration of energy per unit weight. Hence any further effort to conquer outer space must be chiefly aimed at devising new formulas of rocket fuels more efficient than the existing ones. It is pointed out that large-scale application in space rockets of propellants based on fluorine oxidizers and using liquid hydrogen as a fuel will be possible in the near future. Compared with oxygen-base propellants, and especially those based on

nitric acid, these propellants are considerably more powerful. Yet, even fluorine-base propellants are not likely to satisfy the energy requirements for flights to celestial bodies at great distances from the earth.

Utilization of free radicals which in terms of energy exceed tens of times the conventional liquid propellants, will be the next step in the conquest of outer space. Even more tempting is the application to rocket engines of nuclear fuel provided the energy contained in it can be put to full use. The solution of the problem of efficiently using nuclear fuel in rocket engines will at the same time solve the problem of long-lasting manned flights in outer space, i.e., the virtual establishment of interplanetary communications.

Footnotes

- 1 In principle, a third method of obtaining monopropellants is possible. It consists in utilizing the energy of free radicals. At the present time, however, it has no practical value and is therefore not shown in Fig. 1 (see Section 12).
- 2 Latent heat of vaporization is the amount of heat necessary to vaporize 1 kg of liquid heated to boiling point.
- 3 Ideal combustion temperature is propellant combustion temperature without heat losses.
- 4 Polymerization is the process combining several molecules into one large molecule.

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